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SEMINAR ON AIR POLLUTION BY MOTOR VEHICLES, 1967

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Washington, D. C.

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SEMINAR

ON

AIR POLLUTION BY MOTOR VEHICLES

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Washington, D. C.

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A. THE CONTRIBUTION OF MOTOR VEHICLE EMISSIONS TO COMMUNITY-WIDE AIR POLLUTION LEVELS

Included are Emissions from gasoline and diesel engines and photochemical reactions in the atmosphere.

I. General

A. The contribution of motor vehicle emissions to community-wide air pollution depends on a number of related factors: the extent of community, commercial and industrial sources as compared to vehicle sources; the size of the community and the distribution of these sources; topographical and meteorological factors; and the degree of control exercised for these various sources.

The report gives results for different engines and stations in the U.S.

1. The number of cars, or perhaps a better measure, the vehicle miles driven per unit area can of itself create an area-wide problem, e.g., in Los Angeles or Washington, D. C. Or the concentration of vehicles on city streets or expressways with limited ventilation can result in a local problem, e.g., excessive carbon monoxide exposures.

2. Extent of other community sources, e.g., home heating fuels, type of combustion devices, and sulfur content of fuels are important considerations. For example, London's problem concerns high-sulfur coals burned in fireplaces, with fires banked during the night with the result that they become more efficient pollution producers. Another example is that poly-nuclear hydrocarbons in the atmosphere of the United States appear to be associated with the use of coal; it has been found that high levels in the United States cluster around the bituminous coal production and consumption centers. Refuse disposal may be a very important local source in that open dumps, municipally operated incinerators, backyard incinerators, and leaf burning all produce substantial amounts of pollutants.

3. Extent of commercial and industrial sources is obviously an important consideration. The numbers and sizes of these sources, the types of pollutants emitted and controls utilized determine the relative importance of this group of sources.

4. The size of the community and distribution of sources cannot be ignored, in that any localized source, including transportation, can result in a problem.

5. Effect of topography and meteorology are evident, in that these factors control the dispersal of pollutants, e.g., Chicago's problem would be much worse if the "Windy City" had less wind, and Los Angeles' would be better with less topographic shielding, more weather fronts and less large scale anticyclonic subsidence resulting in clear skies with an abundance of sunshine.

6. The degree of control exercised locally determines the relative extent of importance of various sources.

a. The Los Angeles problem is now predominantly auto exhaust, in large part because of increasing control of all other sources while the auto exhaust problem continues to expand. The control of these other sources, including elimination of backyard incineration, has prevented the problem from becoming even greater than now exists.

b. The regulation of fuels, e.g., specifications for volatiles and sulfur and ash content of coal in St. Louis and Pittsburgh not only eliminated the immediate vexing problem of smoke, but opened the door for a look at other less obvious types of pollutants.

c. Regulation of combustion sources generally, i.e., domestic heating, commercial and industrial boilers, power generation, and incineration are important.

d. Industrial source control is obviously important.

e. The use of blow-by and exhaust control devices on automobiles, and enforcement of regulations on smoke from vehicles is again obvious.

B. The determination of the relative importance of motor vehicle emissions can be approached from several directions: (1) evaluation of specific effects, (2) evaluation of specific pollutants in the atmosphere causing effect of interest, or (3) evaluation of all sources with respect to pollutant emissions of all types.

1. Evaluation of specific effects. The recognized effects of motor vehicle emissions, including both irradiated and nonirradiated exhausts, include damage to plants, mucous membrane irritation (eye, nose, throat, and respiratory system) and visibility reduction. Although all of these can and do result from pollutants from other sources, the motor vehicle exhaust has trademarks all its own. The two most recognized are (1) photochemical types of plant damage, and 2) eye irritation and visibility reduction occurring simultaneously with ozone or oxidant production.

a. Manifestations of photochemical smog have been seen and reported in 27 states and the District of Columbia and in Canada, Mexico, and parts of Europe. Geographical distribution ranges from the Pacific Coast States across the country to the Mountain, North and South Central, and East Coast States.

b. In California, air pollution has been reported as affecting 26 of the State's 58 counties.

c. It is to be noted that irradiation is not a neces- ingredient for all effects of vehicle pollution, e.g., ethylene is a pollutant in its own right, and has been a problem in greenhouse operation, particularly orchid production.

2. Evaluation of specific pollutants. Oxidant production is usually direct evidence of photochemical smog. The adverse level associated with odor, eye irritation, plant damage and reduction in visibility is generally considered to be approximately 0.10 to 0.15 ppm (potassium iodide method) or about 0.15 to 0.25 ppm (phenolphthalein method) (1).

a. Results obtained by a simple network of stations in the Washington, D. C. area, as shown in Table A-1, are illustrative of how this type of pollution may be evaluated (2). Oxidant values were determined by the phenolphthalein method with sampling periods of from 10 to 20 minutes; samples were collected between 11 a.m. and 1 p.m.; data are for the period October 1961 - September 1962.

Table A-1

MONTHLY MAXIMUM OXIDANT CONCENTRATIONS IN PPM
Metropolitan Washington, D. C.

Station	Mean	Minimum	Maximum
Alexander, Va.	0.15	0.04	0.26
Arlington, Va.	0.14	0.06	0.26
Beltsville, Md.	0.13	0.05	0.27
Cheverly, Md.	0.11	0.06	0.18
Washington, D.C.	0.16	0.05	0.41
Fairfax, Va.	0.15	0.06	0.28
Rockville, Md.	0.14	0.04	0.39

b. A report by the Public Health Service in 1964 (3) on the automotive air pollution problem summarizes the growing body of data indicating that photochemical smog occurs in communities throughout the United States. It has been estimated that in large metropolitan communities motor vehicles are responsible for a large percentage of the critical precursors to photochemical smog; about 97% of the total olefins, 40 to 80% of the total hydrocarbons, and 14 to 67% of the oxides of nitrogen. Data for oxidant obtained by the Continuous Air Monitoring Program of the Public Health Service (5) indicates that maximum hourly mean values (KI) equalled or exceeded 0.13 ppm and maximum daily mean values equalled or exceeded 0.05 ppm in all cities where such stations are operated. Table A-2 summarizes the data for the period January - December 1964 (4).

Table A-2

HOURLY OXIDANT VALUES AT CONTINUOUS AIR MONITORING STATIONS FOR PERIOD JANUARY-DECEMBER 1964

City	Percent of Days Equal to or Greater Than 0.05 ppm (KI)	0.10 ppm (KI)	0.15 ppm (KI)
Chicago	59	6	0
Cincinnati	45	12	2
Los Angeles	63	42	24
Philadelphia	43	13	3
St. Louis	62	10	2
San Francisco	24	4	1
Washington, D.C.	56	14	1

Oxidant data indicating atmospheric concentrations equal to or exceeding the generally accepted adverse levels have also been reported in the communities shown in Table A-3 (4).

Table A-3

OXIDANT VALUES IN VARIOUS U. S. CITIES

City	Maximum Reported Total Oxidant (ppm)	Method
Atlanta, Ga.	0.14	Phenolphthalein
Birmingham, Ala.	0.20	Pnenolphthalein
Denver, Colo.	0.13	Potassium iodide
Detroit, Mich.	0.27	Potassium Iodide
Jacksonville, Fla.	0.16	Phenolphthalein
Louisville, Ky.	0.58	Potassium iodide
Minneapolis, Minn.	0.39	Potassium iodide
Nashville, Tenn.	0.16	Potassium iodide
Phoenix, Ariz.	0.13	Phenolphthalein
Providence, R. I.	0.27	Phenolphthalein
Spartenberg, N. C.	0.10	Phenolphthalein
Tucson, Ariz.	0.23	Phenolphthalein

It is noted also that carbon monoxide is an excellent source indicator of automobile pollution, and that hydrocarbons and nitrogen oxides are fair in this respect.

3. Source evaluation. Source evaluation may be accomplished to the extent allowed by the availability of manpower and funds for enumerating the individual sources and determining the specific emissions from these sources. This procedure covers the gamut from "shotgun guestimates" to fairly close approximations of the actual situation.

a. A very comprehensive source evaluation has been made for the Los Angeles area (5), as shown in Table A-4. Note in particular the figures on hydrocarbons, carbon monoxide, and nitrogen oxides.

Table A-4

AVERAGE EMISSIONS OF AIR CONTAMINANTS IN TONS PER DAY
LOS ANGELES COUNTY, JANUARY 1965

Emission Source	Hydrocarbon and Other Organic Gases	Aerosols	NO_x	SO_2	CO
Transportation					
Gasoline Powered Vehicles					
Exhaust	1,400	45	490	30	10,300
Blowby	190	-	-	-	30
Evaporation	340	-	-	-	
Total	1,930	45	490	30	10,330
Diesels	8	2	8	2	2
Aircraft, Ships and Railroads	31	12	13	-	151
Substotals(Transportation)	1,969	59	511	32	10,483
Percent of Total (midrange)	71%	46%	65%	10%	98%
Petroleum	220	4	45	45	170
Organic Solvent Use	495	7	-	-	-
Chemical	55	8	-	65	-
Incineration	1	1	1	-	1
Metals	-	8	3	3	3
Minerals	1	7	6	-	-
Miscellaneous Combustion of Fuels	(7-14)	(17-45)	(180-270)	(17-310)	1
Total Range:					
From	2,750	115	745	160	10,660
To	2,755	140	835	455	10,660

b. In a survey of Louisville (6), the data in Table A-5 were determined. Note that transportation accounts for only 6 percent of the total emissions.

Table A-5

AIR POLLUTION EMISSIONS IN LOUISVILLE, KENTUCKY

SOURCE	GASES		SOLIDS		GASES PLUS SOLIDS	
	Tons/ Month	% of all E- mis- sions	Tons/ Month	% of all E- mis- sions	Tons/ Month	% of all E- mis- sions
Transportation	776	6	33	0.1	789	6
Domestic	854	6	366	3	1,220	9
Industry	10,274	78	916	7	11,190	85
Totals	11,904	90	1,295	10.1	13,199	100

c. A survey in Detroit (7) is summarized in Table A-6. Note that motor vehicles account for about 50 percent of the hydrocarbons and a third of the nitrogen ozides.

Table A-6

AIR POLLUTION EMISSIONS IN DETROIT, MICHIGAN

SOURCE	Alde- hydes	Organic Acids	Hydro- carbons	NO_x	SO_x	Other Gases	Solids
Motor Vehicles	30	-	810	130	30	-	-
Other Public Sources	10	230	360	140	410	-	230
Other Industry	10	280	490	170	650	250	1,040
Totals	50	510	1,660	440	1,090	250	1,270

d. A survey of Pennsylvania (8) for eleven counties indicates in Table A-7 the ranges of contributions of pollutants in percent of total. Note that this can be quite variable depending on the particular area of concern.

Table A-7

AIR POLLUTION EMISSIONS IN ELEVEN PENNSYLVANIA COUNTIES
(Ranges in Percent of Total Emissions)

SOURCE	Gaseous	Particulate	Total
Vehicular	18-77	3-66	15-77
Domestic	2-33	2-75	2-37
Industrial	1-92	2-79	2-80

e. Comparative data for Philadelphia (9) and Los Angeles are presented in Table A-8. Note that motor vehicles and commercial transport account for 42% of the total for Philadelphia compared to 70% for Los Angeles. In terms of quantity of emissions Philadelphia has about 570 tons compared to 1278 tons for Los Angeles, or only 45% as much.

Table A-8

SOURCES OF HYDROCARBON EMISSIONS - 1961

SOURCE	Los Angeles			Philadelphia		
	Tons/Day	%		Tons/Day	%	
Motor Vehicle Private	1,038	57	70%	500	37	42%
Commercial Transport	240	13		70	5	
Petroleum Operations	245	13		200	15	
Combustion (Stationary)	5	0		160	12	
Incineration	0	0		150	11	
Industrial Processing	315	17		270	20	
Total (Rounded)	1,840	100		1,350	100	

References (Section A)

1. Technical Report of California Standards for Ambient Air Quality and Motor Vehicle Exhaust, State of California Department of Public Health.

2. Annual Report of the Metropolitan Washington Council of Government's Oxidant Sampling Network, October 1961-September 1962, U. S. Department of Health, Education, and Welfare, Public Health Service, Washington, D. C., October 25, 1962.

3. Automotive Air Pollution, A Report of the Secretary of Health, Education, and Welfare to the U. S. Congress, December 1964.

4. Brice, R. M. and Ludwig, J. H. The Distribution of Vehicular Air Pollution in the United States, Paper No. 65-21, Annual Meeting APCA, Toronto, Canada, June 1965.

5. Chass, R. L. et al., Summary of Total Air Pollution Data for Los Angeles County, January 1965, Air Pollution Control District, County of Los Angeles, California.

6. The Air Over Louisville, Summary of a Joint Report by the Special Air Pollution Study of Louisville and Jefferson County, Kentucky, 1956-57, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio, May 1958, pp. 30-32.

7. Report of the International Joint Commission, United States and Canada, on the Pollution of the Atmosphere in the Detroit River Area, Washington, D. C. and Ottawa, Canada, 1960, p. 70.

8. Anderson, D. M. et al., Pure Air for Pennsylvania, Pennsylvania Department of Health and the Public Health Service, Department of Health, Education, and Welfare, Washington, D. C., November 1961, p. 23.

9. Automotive Air Pollution, A Report of the Panel of Technical Advisors on Automotive Air Pollution to the Joint State Government Commission, General Assembly of the Commonwealth of Pennsylvania, 1963, p. 37.

Section B

Emissions from Gasoline and Diesel Engines

(Outline)

I. Introduction

II. Extent of problem classified by vehicle usage, engine class and fuel consumption.

- A. Classification by vehicle usage
- B. Classification by engine class
- C. Classification by fuel consumption
- D. Interpretation in relation to the vehicle problem

III. Sources of gaseous emissions from motor vehicles

- A. Spark ignition engines
  1. Tailpipe exhaust emissions
  2. Crankcase ventilation losses or blow-by
  3. Evaporation losses
- B. Diesel (compression ignition) engines
  1. Tailpipe exhaust emissions
  2. Crankcase ventilation losses or blow-by
  3. Evaporation losses

IV. General gaseous pollutant types

- A. Gasoline vehicle tailpipe emissions
- B. Gasoline vehicle crankcase emissions
- C. Diesel vehicle tailpipe emissions
- D. Gasoline vehicle evaporation losses
- E. Summary

V. Specific pollutant types

- A. Gasoline vehicle tailpipe emissions
- B. Gasoline vehicle crankcase emissions
- C. Gasoline vehicle evaporation losses
- D. Diesel vehicle tailpipe emissions
  1. Hydrocarbon emissions
  2. Smoke emissions
  3. Irritant and odorous emissions
  4. California standards for vehicle smoke emissions

VI. In-traffic carbon monoxide levels

VII. Particulate emissions from vehicles

VIII. California standards for nitrogen oxides emissions from vehicles.

IX. Summary for Section B - References (Section B)

B. EMISSIONS FROM GASOLINE AND DIESEL ENGINES

I. Introduction The role of various types of motor vehicles in the atmospheric pollution depends on a number of factors, all of which must be considered in any control program.

1. Extent of problem classified by vehicle usage, engine class, and fuel consumption.
2. Sources of emissions from motor vehicles.
3. General pollutant types.
4. Specific pollutant types emitted.
5. Significance of pollutant types in a practical control program.

II. Extent of problem classified by vehicle usage, engine class, and fuel consumption. Data from California will be used to illustrate the general aspects of the problem.

A. Classification by vehicle usage (1).

a. Of 8,000,000 motor vehicles registered in California in 1960, approximately 1,000,000 werecommercial trucks, 6,000 were commercial buses, and 5,700 were noncommercial buses, for a total of 12.7 percent trucks and buses.

b. Of the total trucks and buses, about 70% were gasoline-powered trucks with an unladen weight of under 6000 pounds Including this lightest category of trucks with passenger cars, the breakdown of vehicles in California is shown in Table B-1 (2). Note that the total percentage of trucks and buses over 6000 pounds unladen weight is 3.68%.

Table B-1

CALIFORNIA VEHICLE POPULATION BY TYPE, GROSS WEIGHT AND ENGINE DISPLACEMENT FOR VEHICLES UNDER 6000 POUNDS

Type, Weight and Engine Displacement	% of Total
Total passenger cars & trucks under 6000 pounds	96.3
Engine displacement ≤ 140 cu. in.*	(7.7)
Engine displacement > 140 cu. in.	(88.6)
Total trucks & buses over 6000 pounds	3.7
Gasoline-powered trucks over 6000 pounds	(3.19)
Gasoline-powered buses	(0.14)
Diesel trucks over 20,000 pounds	(0.32)
Diesel buses	(0.03)

* Roughly 8% of total passenger cars and trucks under 6000 pounds.

B. Classification by engine class (1).

a. Of the 1,000,000 commercial trucks and 6,000 commercial buses, approximately 24,000 and 2,600 respectively, or about 2.6 percent, were diesel-powered. This is 1/3 of 1 percent of all motor vehicles.

b. Of the 11,700 commercial plus noncommercial buses, 2,600 or 22 percent of the total are diesel-powered. However, 2,600 of 6,000 commercial buses or 43 percent are diesel-powered.

c. Registration data on diesels must be supplemented by data on diesel trucks registered outside the state but operating in California. It is estimated that vehicles registered in California represent about one-third of the total diesel traffic in California. Note, however, that this is total traffic and not urban traffic.

d. In California most diesel trucks have Cummins (four-stroke) engines and most diesel buses have General Motors (two-stroke) engines.

e. In California Cummins engines comprise 70 percent of the California diesel population and General Motors engines are the remaining 30 percent.

C. Classification by fuel consumption (1).

a. In California in 1960, 5,700 million gallons of gasoline, 280 million gallons of diesel fuel, and 27 million gallons of LPG fuel were sold in California for vehicle use; diesel fuel amounted to 5 percent of the total.

b. It is estimated that in Los Angeles County, two-thirds of the diesel fuel sold is used in long-haul operations outside of the county. Hence only about 1-1/2 percent of the motor vehicle fuel sold in Los Angeles is used by diesels in urban travel.

D. Interpretation in relation to the vehicle problem.

a. These figures on population give only a general estimate or a range of the problem involved with various types of vehicle. It must be kept in mind that determination of fuel usage by vehicle type, power plant type, and location is not amenable to precise methods of estimation.

b. The extreme complexity of the problem explains to a large degree public misunderstanding of the problem, or the way control is being implemented.

c. Direct transfer of the California data to other locations in the country is hazardous; in general, however, the situation in California can be used as a basis to roughly assess the problem elsewhere.

d. A general conclusion from these data is that passenger cars and trucks under 6000 lbs. gross weight constitute the largest single group source of vehicle emissions; this does not imply that other types of vehicles do not produce pollutants, nor that these may not constitute special problems, nor that all sources should not be brought under control.

III. Sources of gaseous emissions from motor vehicles.

A. Spark ignition engines. Three sources of emissions from spark-ignition engines rank as folllows, on the basis of hydrocarbon emissions:

1. Tailpipe exhaust emissions (50-60 percent)

a. Since tailpipe exhaust emissions are the major quantitative source of automotive emissions, and the most important "species-wise" in relation to photochemical smog, major emphasis has been placed on investigations of this source ranging from research into the basic chemical processes involved in photochemical smog to control of these emissions.

b. Efforts to reduce exhaust emissions have involved enormous expenditures by private enterprise and government agencies, principally the former, over the past 10 years.

c. Methods being investigated involve a number of approaches ranging from modifications in the engine design to tailpipe appurtences to reduce emissions.

d. Tailpipe appurtences involve either devices promoting low-temperature combustion by use of a catalyst or an afterburner designed to produce temperatures high enough to operate at the extremely low quantities of combustibles contained in exhaust. It is noted that high exhaust concentrations from an air pollution standpoint are on the extremely low side compared to normal gaseouls fuel-air combustion mixtures.

e. Performance and life testing of a number of tailpipe exhaust control devices has been carried on in California for a number of years. As of January 1, 1965 (3), 43 applications for exhaust control systems had been received, of which 34 were rejected or withdrawn. From the nine applications remaining four tailpipe devices have been approved, three catalytic (for new cars only) and one direct-flame (for both new and used cars). Four additional catalytic devices were under test at that time for use on new cars. The approval of four devices for new cars on June 17, 1964 by the Motor Vehicle Pollution Control Board made mandatory the provision of exhaust control devices for all new cars sold in California starting with the 1966 model year. One of these devices was approved for both new and used vehicles. Activities on development of this type

of device has been sharply curtailed since June 1964, however, due to the decision of the automobile manufacturers not to utilize tailpipe appurtenances for 1966 vehicles built to meet present State of California exhaust standards. (See f below) There is still interest in this type of device for use under much more restrictive standards than those presently proposed, or for the used car market. It is noted that certification of tailpipe devices was withdrawn for the four devices previously approved by the MVPCB in 1965 due to the passage of additional legislation withdrawing the possibility of annual servicing.

f. The approval of devices on June 17, 1964 was followed closely on August 12, 1964 with announcements from four major automobile companies that they would be able to comply with the California law requiring approved exhaust systems on 1966 model cars. The systems to be used would not be tailpipe appurtenances but would employ basic engine modifications. These are discussed in g and h below.

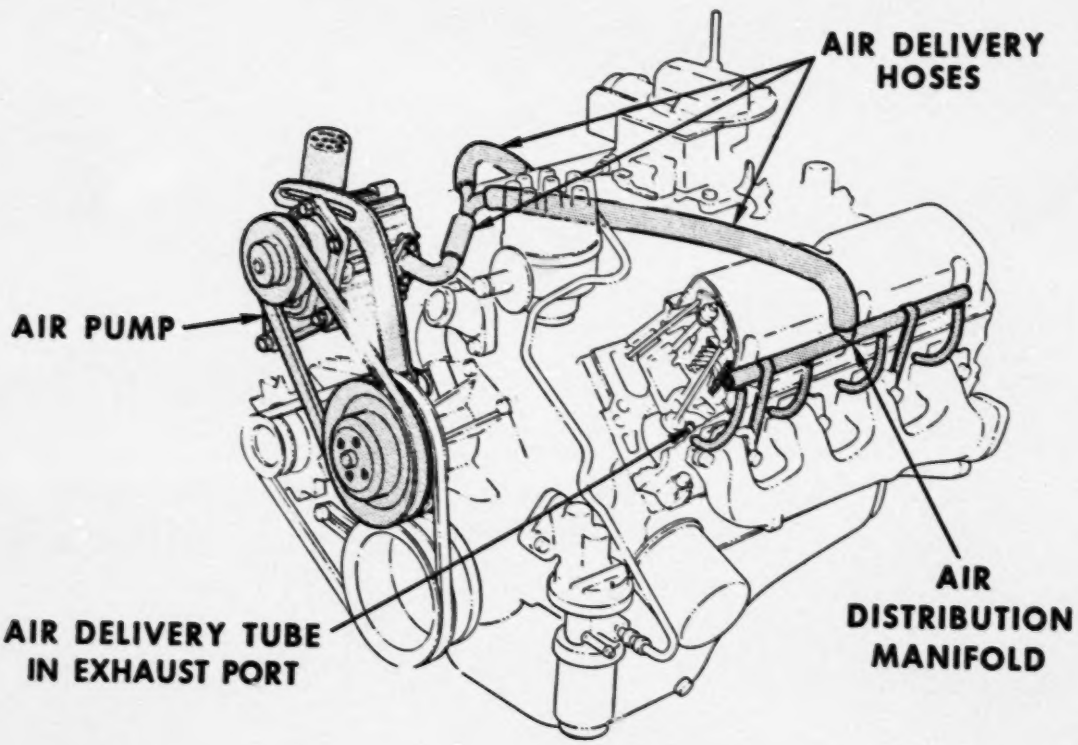
g. The device used on Chrysler products involves modification of the induction system. In principle it incorporates the advantages of lean carburetion operation coupled with spark retardation at low speeds or idle which increases the combustion time during low-load low-speed conditions when hydrocarbon concentrations are normally high. Other optimization features have, of course, been incorporated into the design. This control system is called the "Cleaner Air Package," Some 1967 models of General Motors, Ford and American Motors employ a similar system.

h. Ford, General Motors and American Motors for 1966 model-year cars adopted a method to control exhaust emissions that utilizes, for the most part, injection of air at the cylinder exhaust ports. This accomplishes two ends: (1) high-temperature combustion of hydrocarbons and carbon monoxide in the exhaust manifold while the temperatures of the exhaust are still relatively high, and (2) prevent dilution of the fresh air-fuel cylinder charge with exhaust back-flowing through the exhaust valve. The latter occurs primarily during low-speed operation due to valve overlap requirements for high power at high speed. The Ford system is called "Thermactor", the General Motors system "Air Injection Reactor", and the American Motors system "Air Guard". The principle of these systems is illustrated by the Ford "Thermactor" system shown in Figure B-1.

i. The federal government entered the vehicle emissions control picture when Congress passed Amendments to the Clean Air Act, Pl. 89-272, on October 20, 1965. This law requires the Department of Health, Education, and Welfare to set standards for vehicle emissions which will be applicable nationwide. On March 31, 1966, proposed standards to be effective for 1968 model-year cars were published in the Federal Register. These standards are those applicable to State of California 1966 model-year cars: exhaust emissions not greater than 275 ppm and CO not greater than 1.5% for cars

FIGURE B-1

FORD THERMACTOR EXHAUST EMISSION CONTROL SYSTEM



with engines exceeding 140 cubic inch displacement. The adoption of the California standards for nationwide application was influenced by the capability of the automobile industry to produce cars with control devices, considering that production today is over 10,000,000 cars and trucks per year, and that tool-up is for 1968 model-year cars starts 20 months before the model is introduced, or January 1966. The federal standards also include requirements for imported cars which are less stringent on an exhaust concentration basis due to the lower volume of exhaust from vehicles with small engines. These standards are 410 ppm hydrocarbons and 2.3% CO for engines in the 50 to 100 cubic inch displacement class, and 350 ppm hydrocarbon and 2.0% CO for the 100 to 140 cubic inch class.

j. Other methods proposed for exhaust emission control range from modifications of fuel composition, to optimization of engine design parameters involving factors such as ignition, engine timing, combustion chamber design, fuel carburetion and distribution, fuel injection, lean mixture operation, etc. It is noted that many of these have been adopted in the present systems used by American automobile manufacturers.

k. Long-range control envisions the development of new type power plants with essentially no emissions as we know them today. The turbine engine, stratified-charge engines, electric-powered cars, and fuel cells are examples of such developments and concepts.

2. Crankcase ventilation losses or "blow-by" (30-40 percent) (Figures B-2 and B-3)

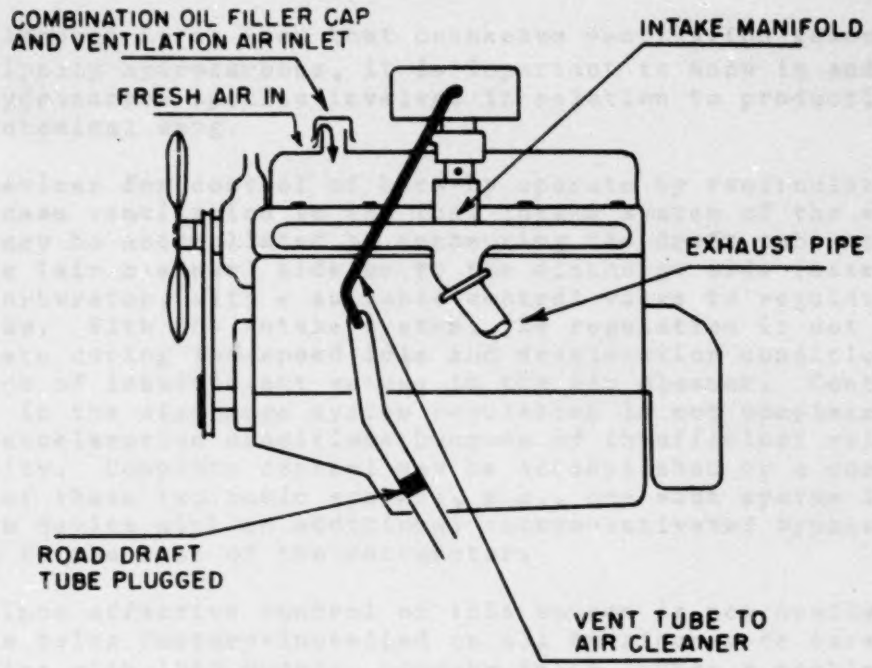
a. Blow-by consists of a mixture of unburned fuel-air charge and exhaust products "blown" past the piston rings during the compression and power strokes of the engine cycle.

b. Blow-by is diluted with crankcase ventilation air, which enters the crankcase through the oil filter cap. This air blow-by mixture, prior to the use of crankcase emission control devices, was discharged through the engine draft tube.

c. During the dilution process in the crankcase, there is probably an interchange of blow-by constituents in the engine oil, combined perhaps with the vaporization of the lighter hydrocarbons in the oil itself.

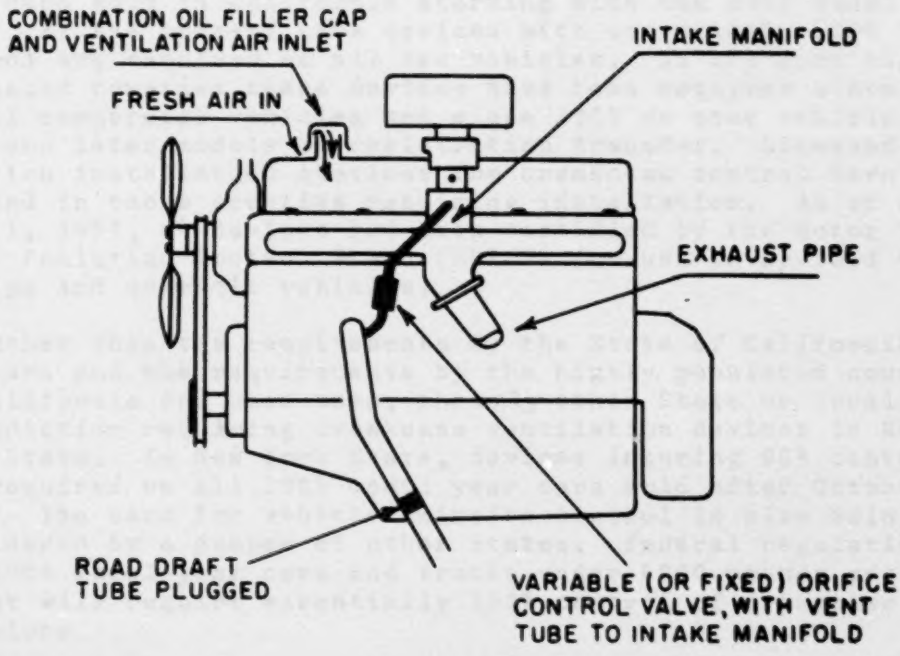
d. Examination of CO-CO_2 relationships indicates the composition of blow-by to be 75-85 percent carbureted fuel and 25-15 percent combustion products.

e. Concentration of hydrocarbons varies between 10,000-12,000 ppm carbon. To satisfy the CO-CO_2 relationship this should be around 15,000 ppm carbon, which leads to the conclusion that the blow-by is significantly modified in the crankcase by contact with the engine oil.



VENT TUBE TYPE CONTROL SYSTEM

FIGURE B-2



VARIABLE ORIFICE METERING CONTROL SYSTEM

FIGURE B-3

f. Although it is know that crankcase ventilation gases are principally hydrocarbons, it is important to know in addition the hydrocarbon species involved in relation to production of photochemical smog.

g. Devices for control of blow-by operate by recirculating crankcase ventilation to the fuel intake system of the engine. This may be accomplished by connecting the draft tube to the intake (air cleaner) side or to the discharge side (base) of the carburetor, with a suitable control valve to regulate airflow. With the intake system, the regulation is not complete during low-speed idle and deceleration conditions because of insufficient vacuum in the air cleaner. Contrariwise, in the discharge system regulation is not complete during high-acceleration conditions because of insufficient valve capacity. Complete control may be accomplished by a combination of these two basic systems, e.g., one such system is the intake device with an additional vacuum-activated bypass valve to the base of the carburetor.

h. Since effective control of this source is now available and is being factory-installed on all American-made cars sold starting with 1963 models, blow-by is no longer a problem as an individual source. Proper maintenance is, of course, necessary

i. The Motor Vehicle Pollution Control Board of the State of California has been certifying devices for a number of years, and these devices were required on all new American-made cars sold in California starting with the 1961 model year. At the present time devices with essentially 100% control are required on all new vehicles. In the more highly populated counties these devices have been required since 1964 on all commercial vehicles and since 1965 on used vehicles for 1955 and later models on registration transfer. Licensed inspection installation stations for crankcase control have been adopted in those counties requiring installation. As of January 1, 1967, 64 devices had been certified by the Motor Vehicle Pollution Control Board (MVPCB) for use on new and used, foreign and domestic vehicles.

j. Other than the requirements by the State of California for new cars and the requirements by the highly populated counties in California for used cars, the only other State or local jurisdiction requiring crankcase ventilation devices is New York State. In New York State, devices insuring 80% control are required on all 1965 model year cars sold after October 1964. The need for vehicle emission control is also being considered by a number of other states. Federal regulations for 1968 model-year cars and trucks under 6000 pounds gross weight will require essentially 100% control of crankcase emissions.

3. Evaporation losses (15-25 percent). These losses come from two sources: fuel tank and carburetor evaporation.

a. Fuel tank losses occur by displacement of vapor during filling of the gas tank, or by vaporization of fuel in the tank forcing the vapor through the breather vent to the atmosphere.

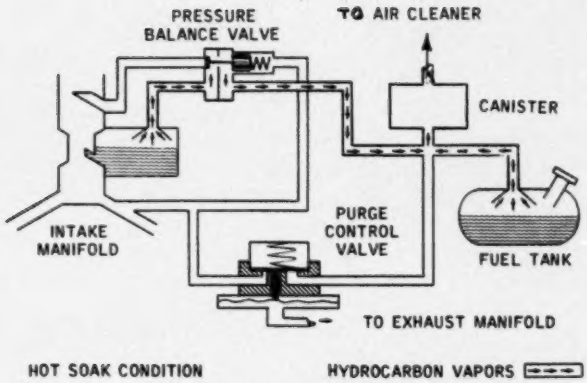
b. Carburetor losses result from (a) external venting of the float bowl to relieve interval pressure as the carburetor heats, and (b) "hot soak" losses, which occur after the engine has been stopped as a result of evaporation of gasoline stored in the bowl.

c. These losses are almost entirely gasoline constituents, favoring of course the more volatile components. Of the various additives used in motor fuels, alkyl lead additives are of most concern; however, since these (TEL and TML; and mixed reaction products) are less volatile than gasoline, their percentage in the vapor is much less than their percentage in the gasoline.

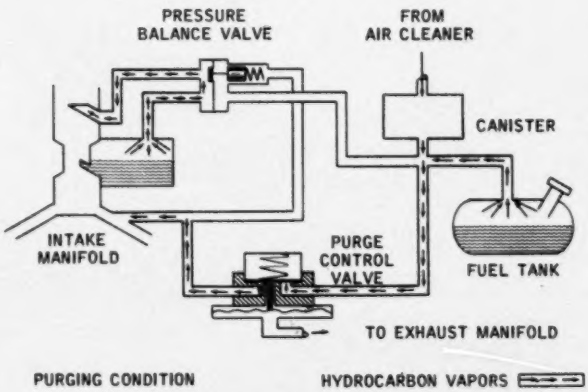
d. Control means for these losses are available, but because of their limited over-all contribution, emphasis in the past has been on control of major sources. To further assist in the alleviation of the smog problem in California, the State Health Department, on October 23, 1964, set standards for fuel tank evaporation and hot soak losses. These standards require an 80% reduction in estimated losses; and limit fuel tank emissions to 6 grams per day of hydrocarbons and carburetor hot soak emissions to 2 grams of hydrocarbons per soak. These emissions are therefore subject to action by the MVPCB, and when two systems for control have been certified by the Board, they will be required in California. Test procedures for certification were adopted by the MVPCB on November 16, 1966. However, no applications for certification of devices have been made as yet.

e. The most promising device for control of evaporative emissions has been developed by ESSO Research and Engineering (11). This device, shown in Figure B-4, consists of a pipe and valve system for venting the fuel tank and the carburetor float bowl to the atmosphere through an activated charcoal cannister where the hydrocarbons are adsorbed. During certain cycles of engine operation as regulated by the purge control valve, i.e., those cycles when the intake air demand is high, hydrocarbons are desorbed from the charcoal by air, metered through a sonic orifice, which passes in reverse through the cannister into the engine manifold.

On February 5, 1967 proposed standards for control of fuel tank and carburetor evaporative emissions were announced by the Secretary of the Department of Health, Education, and Welfare to become effective on 1969 model-year gasoline-powered vehicles under 6000 pounds gross weight. These proposed standards were published in the Federal Register dated February 4, 1967.



BASIC EVAPORATIVE LOSS CONTROL SYSTEM — HOT SOAK CONDITION



BASIC EVAPORATIVE LOSS CONTROL SYSTEM — PURGING CONDITION

FIGURE B-4

4. Diesel (compression ignition) Engines.

1. Tailpipe exhaust emissions comprise essentially 100 percent of the emissions from diesel engines. These amount to about 2 percent of the supplied fuel.

2. Crankcase ventilation losses.

a. Crankcase ventilation losses depend on the type of engine, i.e., two- or four-cycle. Emissions are zero for the two-cycle engine since the combustion air enters from near the base of the cylinder and any blow-by becomes mixed with the inlet air on the next stroke.

b. For the four-cycle engine, crankcase emissions amount to not over 0.05 percent of the fuel, or not over 2-1/2 percent of the total diesel emissions.

3. Evaporation losses are quite low compared to those from gasoline-powered vehicles. Diesels have a closed system of fuel injection instead of carburetion, and diesel fuel is less volatile than gasoline.

IV. General gaseous pollutant types. The discussion thus far has indicated that the emissions of principal interest in the vehicle pollution problem, in the order of their over-all significance, are the following: (1) gasoline-vehicle tailpipe exhaust, (2) gasoline-vehicle crankcase ventilation, (3) diesel-vehicle tailpipe exhaust, and (4) gasoline vehicle evaporative losses. First let us examine the general pollutant types contained in these emissions.

A. Gasoline-vehicle tailpipe emissions.

1. Principal constituents and their relative proportions in the exhaust in ppm for various operating modes of the car are typical of those summarized in Table B-2 (4) for a field survey involving a number of automobiles.

Table B-2

GASOLINE-ENGINE VEHICLE EMISSIONS (ppm) - BREAKDOWN BY ENGINE CYCLE

Constituent	Idle	Cruise	Acceleration	Deceleration
Carbon Monoxide	64,000	24,000	24,000	45,000
Hydrocarbons	1,400	620	810	5,700
Oxides of Nitrogen	0	1,400	1,700	0

2. Hydrocarbons are expressed as hexane and measured by a nondispersive infrared instrument sensitized with hexane and corrected for instrument response to give absolute values.

3. Carbon monoxide and hydrocarbons generally are higher during light-load engine demand, i.e., idle and deceleration.

4. Oxides and nitrogen are higher during heavy-load engine de-demand, as might be expected at the higher temperatures involved, i.e., during cruise and acceleration.

5. The values vary widely, and the average output of any car depends not only on the characteristics of the engine but on the routes and driving conditions, e.g., traffic, weather, etc.

6. To give an idea of the general over-all emissions, road tests made over typical driving routes in Cincinnati with a proportional sampler indicate "average" exhaust composition as shown in Table B-3 (4). Hydrocarbons were measured with a flame ionization detector and are expressed as hexane for comparison with Table B-2.

Table B-3

GASOLINE-ENGINE VEHICLE EMISSIONS (ppm) - BREAKDOWN BY DRIVING ROUTE

	Hydro-carbons	Nitrogen Oxides	Carbon Monoxide
Freeway	360	1,350	31,800
Business	560	760	53,700
Residential	420	980	38,100
Arterial	510	1,290	40,300

7. As would be expected from the previous data, the freeway condition representing a predominance of cruise is low in hydrocarbons and carbon monoxide and high in nitrogen oxides. The business route, representing stop-and-go driving reflects idle and deceleration with high hydrocarbons and carbon monoxide. Residential and arterial routes do not consistently reflect any particular engine cycle.

8. Although data on concentration of pollutants in exhaust for various cycles or driving routes are important for understanding of the basic variables involved, the crux of the matter lies in the total quantities of pollutants produced per mile of travel or useful work accomplished by the vehicle. Figures B-5 through B-8 indicate data secured by measurements on the road over various driving routes in Cincinnati, Los Angeles, and Denver (5), and have been selected for the reason that average route speed appears to be the most important single variable relative to over-all emissions from a vehicle on a "mile traveled" basis. Average route speed appears to reflect engine power demands and consequent pollutant emissions associated with acceleration, deceleration, cruise, and idle driving modes imposed by a multitude of driving variables such as type of route, topography, traffic density, climate, etc.

9. Figure B-5 for the 20 cars surveyed in Cincinnati indicates that, although the variability between vehicles is quite large, each individual car exhibits generally a consistent trend of reduction of emissions with increase in average vehicle speed over various types of routes.

10. Figure B-6 indicates that variability in hydrocarbon emissions with speed for Los Angeles and Cincinnati is quite comparable; values for Denver shows the same trend but indicate higher hydrocarbon emissions resulting from carburetor enrichment due to altitude. Figure B-6 is expressed as pounds of hydrocarbon (computed as $CH_{1.85}$) per mile as measured by a hexane-sensitized nondispersive infrared analyzer.

11. Figure B-7 shows hydrocarbon emissions similar to Figure B-5 except that hydrocarbons were measured using a flame ionization analyzer, an instrument that is much more responsive to all hydrocarbon species. This figure is included to emphasize the need to indicate the instrument used as well as the specific values measured. Values obtained with the flame ionization analyzer usually are roughly double those obtained with the hexane-sensitized nondispersive infrared instrument.

12. Figure B-8 again indicates that carbon monoxide values for Cincinnati and Los Angeles are comparable, while those for Denver are about double the sea-level values, again reflecting the carburetor enrichment at higher altitudes. At altitudes of 11-12,000 feet carbon monoxide emissions are roughly three times those at sea level, a difference that is quite important in the ventilation requirements for high-altitude vehicular tunnels.

13. The fact that for each individual vehicle, the emissions per mile decrease with average route speed, leads to the conclusion that all practical measures should be taken to expedite the flow of traffic in urban areas, since this will, in itself, accomplish significant reduction in vehicle pollution emissions.

B. Gasoline-vehicle crankcase emissions.

1. As previously mentioned, crankcase ventilation emissions consist of about 75-85 percent carbureted fuel, and hence are hydrocarbons of the types contained in the gasoline blend being used for fuel.

2. About 15-25 percent of crankcase emissions are combustion products and hence reflect constituents previously described for exhaust.

3. Confusing the simple picture is the modification of the blow-by by its residence in the crankcase and intimate contact with the engine oil, resulting in a net loss of hydrocarbons and perhaps an interchange of hydrocarbon species between the blow-by and the oil.

4. Generally, however, crankcase ventilation gases consist principally of hydrocarbons.

POUNDS OF GROSS HYDROCARBONS (FIA)
EMITTED PER MILE
VERSUS
AVERAGE ROUTE SPEED
(LOS ANGELES RANDOM VEHICLE SAMPLE)

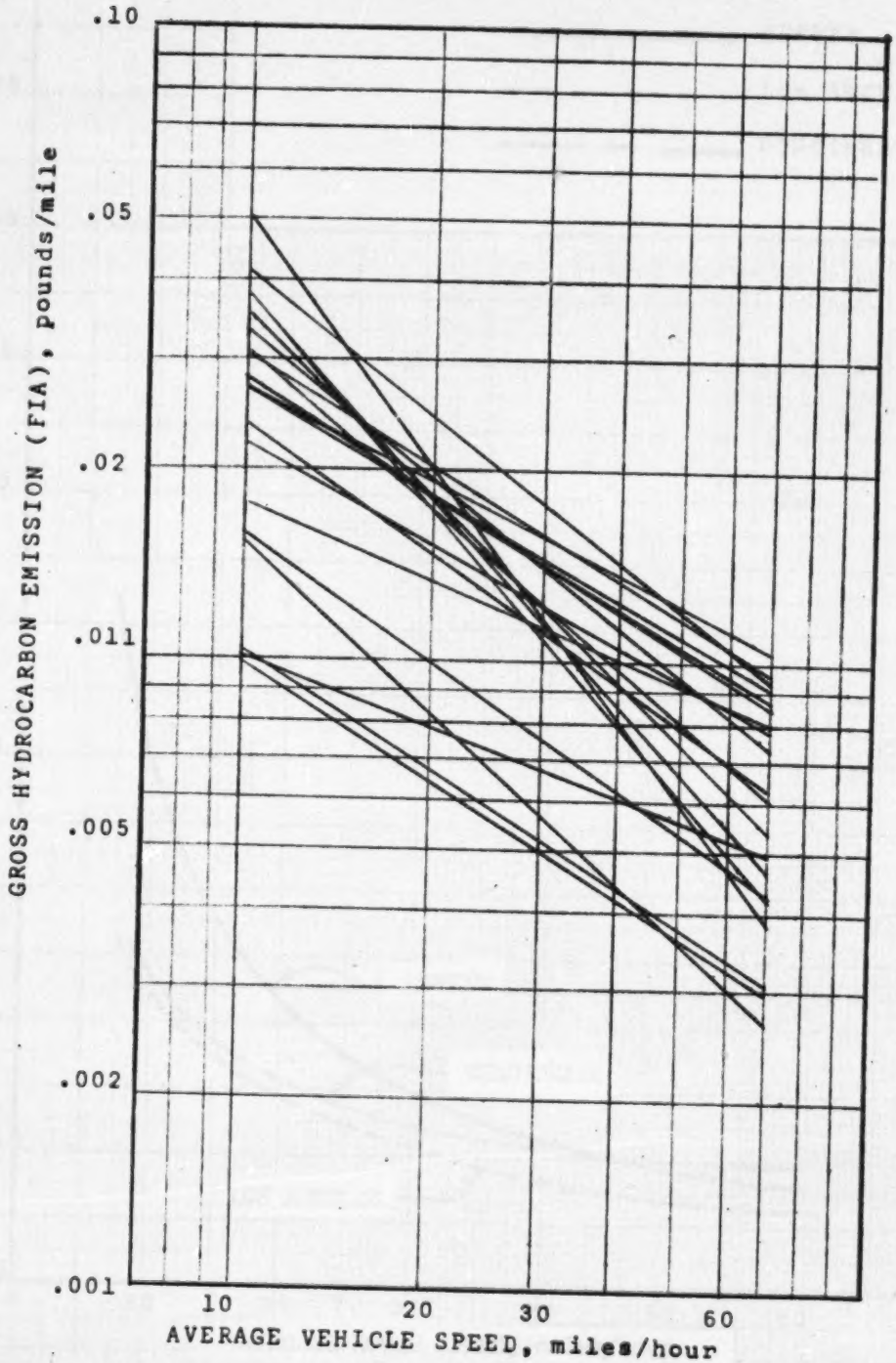


FIGURE B-5

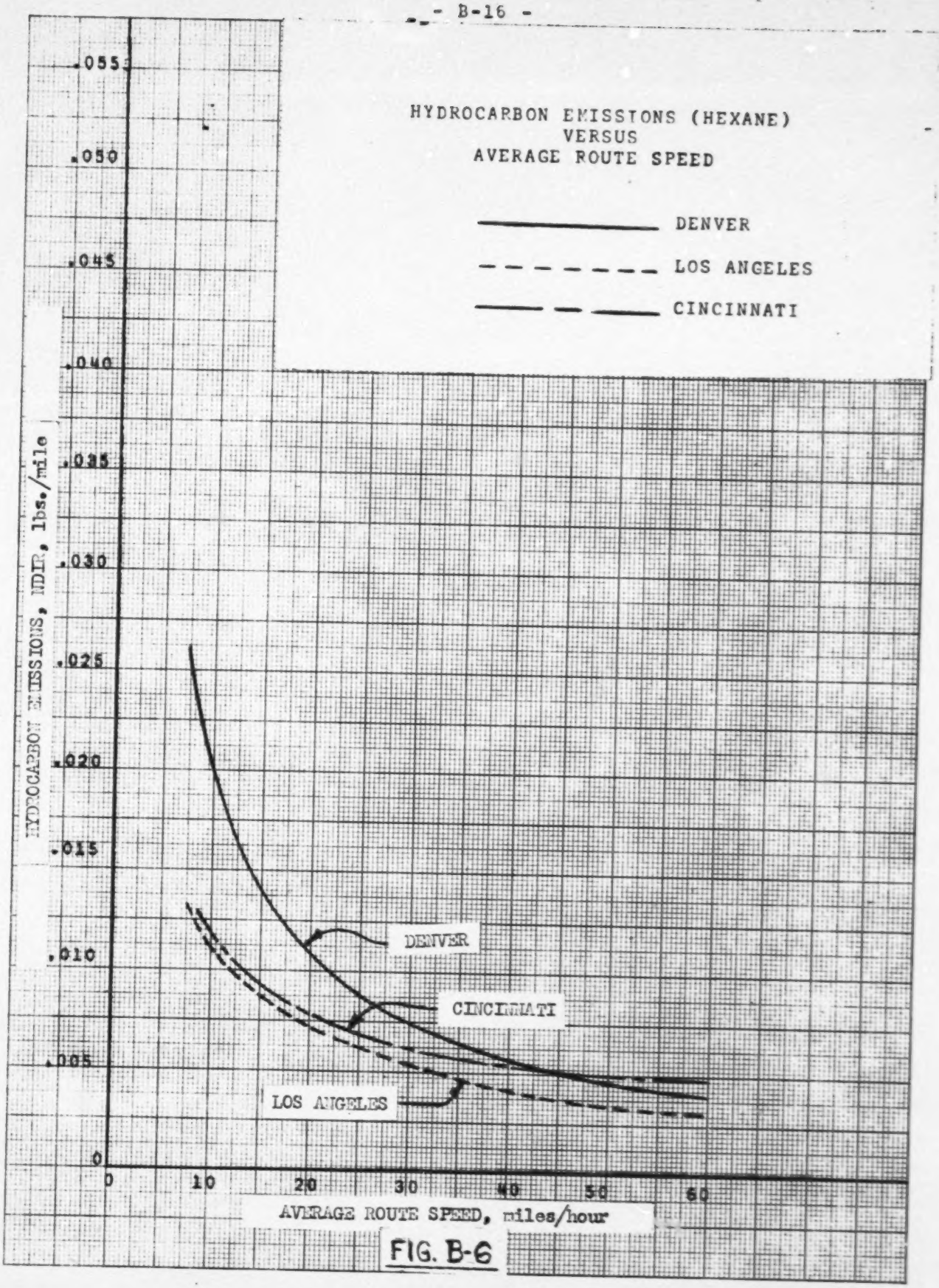

HYDROCARBON EMISSIONS (HEXANE)
VERSUS
AVERAGE ROUTE SPEED
DENVER
LOS ANGELES
CINCINNATI
HYDROCARBON EMISSIONS, MDR, lbs./mile
.055
.050
.045
.040
.035
.030
.025
.020
.015
.010
.005
0
0
10
20
30
40
50
60
AVERAGE ROUTE SPEED, miles/hour
DENVER
CINCINNATI
LOS ANGELES

FIG. B-6

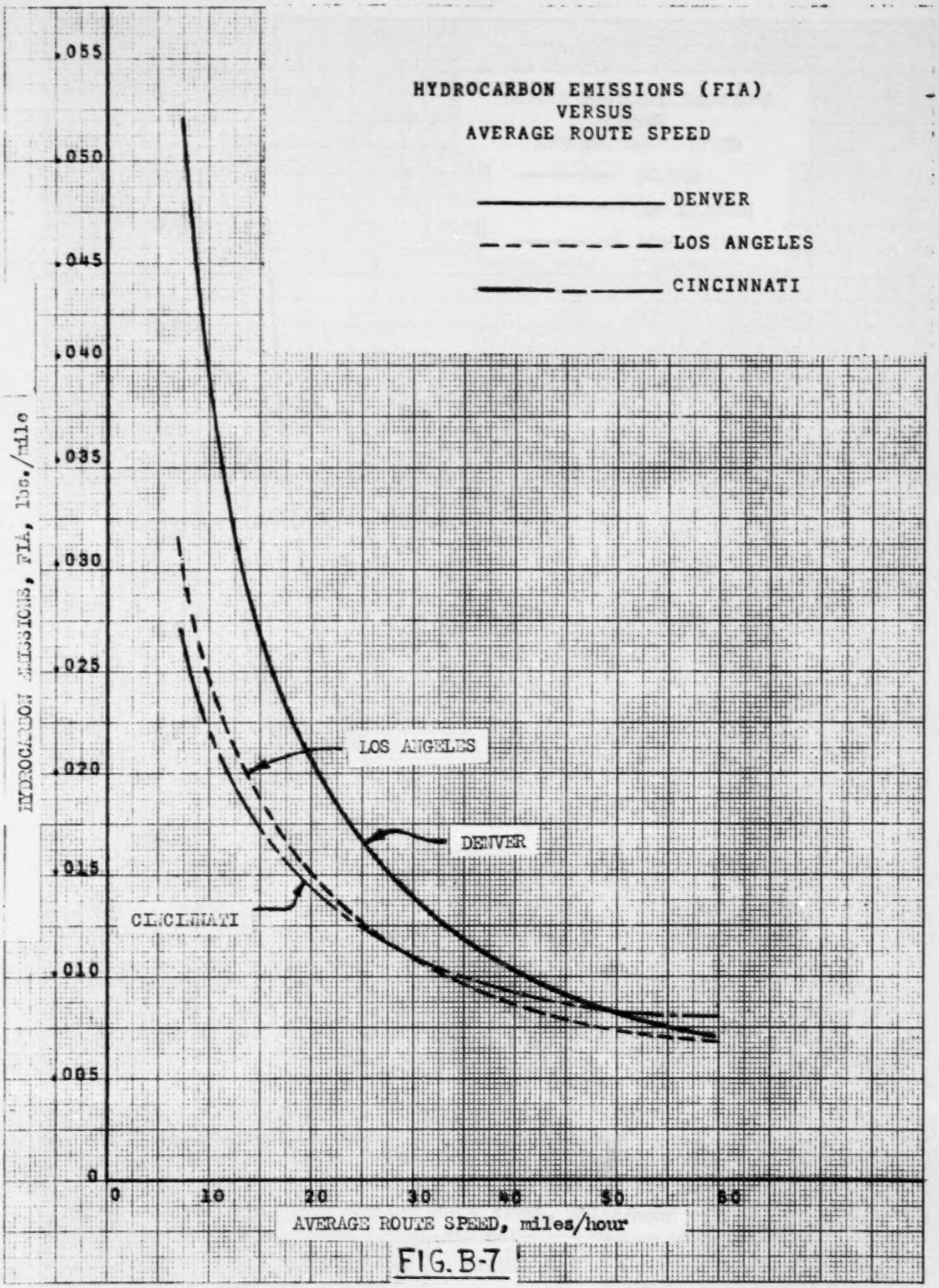

HYDROCARBON EMISSIONS (FIA)
VERSUS
AVERAGE ROUTE SPEED
DENVER
LOS ANGELES
CINCINNATI
HYDROCARBON EMISSIONS, FIA, lbs./mile
.055
.050
.045
.040
.035
.030
.025
.020
.015
.010
.005
0
0
10
20
30
40
50
60
AVERAGE ROUTE SPEED, miles/hour
LOS ANGELES
DENVER
CINCINNATI

FIG. B-7

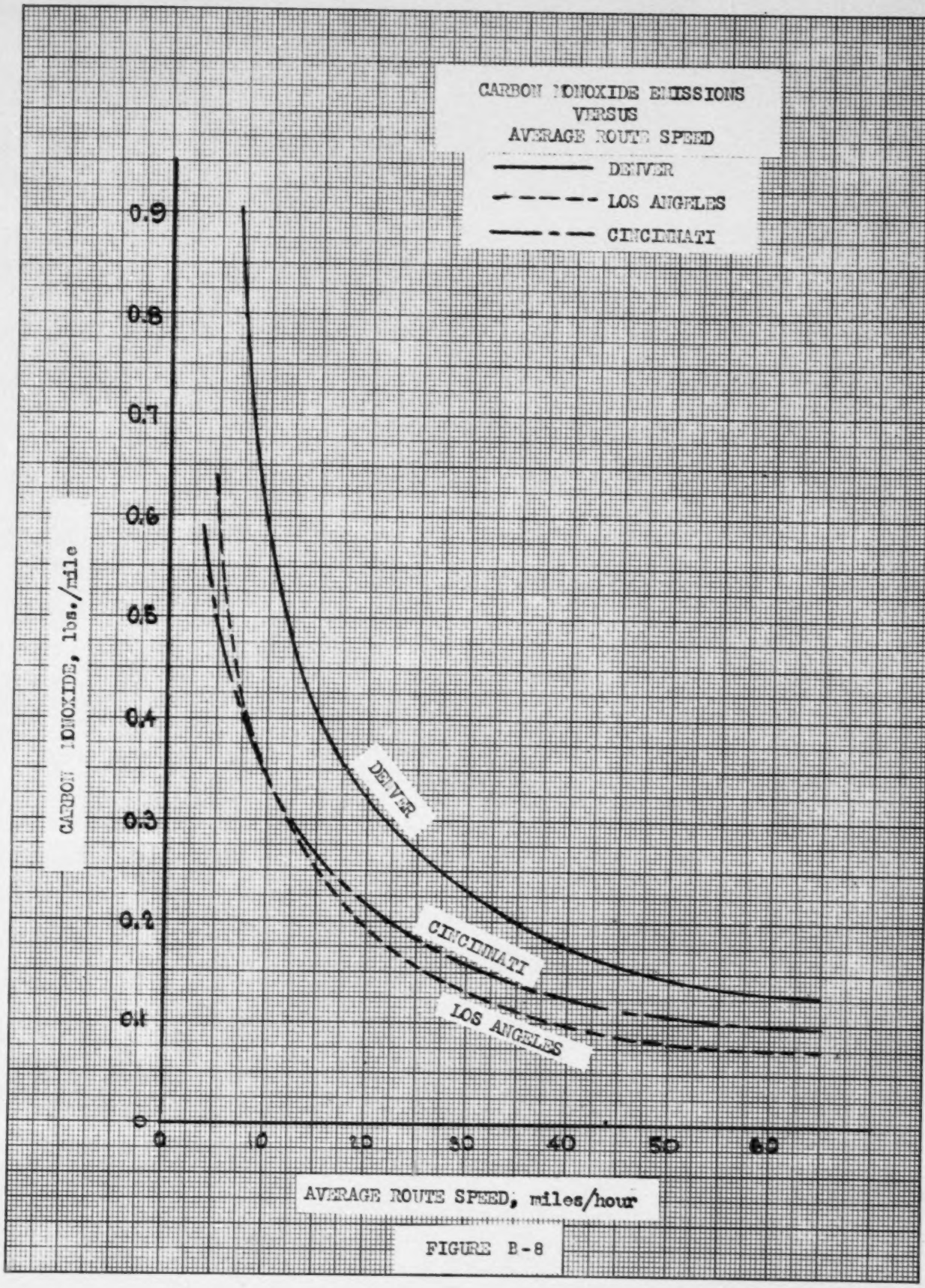


FIGURE B-8

KEUFFEL & ESSER CO., N. Y. NO. 359-14
Millimeters, 5 mm. lines accented, cm. lines heavy
MADE IN U. S. A.

C. Diesel-vehicle tailpipe emissions.

1. As noted previously, diesel engines are of two general types: The two-stroke (e.g., General Motors) engine used in buses; and the four stroke (e.g., Cummins) used in trucks. Air flow and emission data (hydrocarbon, CO, NO_x, and CO_2) are shown in Table B-4 for various load conditions at rated speed (about 50 mph) and for idle (4). Hydrocarbons were measured by a flame ionization detector (ppm carbon), CO and CO_2 by nondispersive infrared and NO_x by a colorimetric method. Emissions are listed by ppm or % by volume and on the basis of lbs./minute.

2. Two-stroke vs. four-stroke. Note that the two-cycle engine emits much higher hydrocarbons under all conditions cited, and more CO and NO_x except for the full load condition.

3. Load vs. idle. Note that hydrocarbons and CO are highest under load conditions and lowest for idle as contrasted to the gaosline powered vehicle. However, NO_x increases with increased load as it does for gasoline powered vehicles.

4. Carbon monoxide. Note that carbon monoxide levels are quite small compared to gasoline powered vehicles, e.g., under the worst conditions 9.2% (2000 ppm) compared to a range of 24,000 to 64,000 ppm listed in Tables B-2 and B-3. The reason for the low CO emissions is that large quantities of excess air are provided in contrast to spark-ignition engines, which operate on air insufficient to produce complete combustion. Diesel exhaust without control devices will meet present State of California and Federal standards of 1.5% (15,000 ppm). A comparison of mass emission basis with gasoline powered passenger cars driven over a typical route at about 25 mph (which admittedly is quite precarious in that one is comparing vehicles of two grossly different weight classes) indicates hydrocarbons from passenger vehicles of about 1500×10^{-4} lbs./ min. (Fig. B-8) compared to a range of 17 to 275 in Table B-4 for diesels. The greater air flow for diesels reduces some of the difference noted on a concentration basis.

5. Hydrocarbons. Hydrocarbon values are also comparatively low compared to spark-ignition engines, the worst condition listed being 605 ppm carbon or 101 ppm (Hexane) compared to a range of 360 to 5,700 ppm (Hexane) shown in Table B-2 and B-3. Diesels without control devices will meet present State of California and Federal standards of 275 ppm (Hexane). Comparision with passenger cars at 25 mph (Fig. B-7), as in item C-4 above, indicates 125×10^{-4} lbs./min. for the passenger car compared to a range of 3.5 to 62.7 in Table B-4 for diesels. Again the greater air flow in diesels closes the gap between emissions compared on a concentration to a mass basis.

6. Nitrogen oxides. Nitrogen oxides emissions in diesels range from 109 to 921 ppm in Table B-4 compared to 760 to 1,700 ppm listed in Tables B-2 and B-3. The present California standard is 350 ppm. Comparison with passenger cars (4) indicates emissions of 33×10^{-4} lbs./min. for passenger cars compared to a range

Table B-4

SUMMARY OF DIESEL EMISSIONS

Operating Conditions	Engine Type	Unit: Air Flow SCFM	Air Flow #1Min	CO_2 %	CO_2 #1Min	HC PPMC	HC #1Min 10^{-4}	CO %	CO #1Min 10^{-4}	NO_x PPM	NO_x #1Min 10^{-4}
1. Full Load Rated Speed*	2-cycle	287	21.3	6.0	1.94	467	48.5	0.1	200	622	202
	4-cycle	187	14.3	10.6	2.40	29	2.0	0.2	275	921	210
2. Half Load Rated Speed*	2-cycle	284	21.7	3.6	1.18	605	62.7	0.03	63	392	135
	4-cycle	204	15.6	5.2	1.24	68	5.2	0.03	45	493	122
3. No Load Rated Speed*	2-cycle	282	21.6	1.5	0.50	530	54.8	0.03	62	147	50
	4-cycle	197	15.1	1.2	0.27	73	5.2	0.03	44	109	26
4. Idle	2-cycle	76	5.9	1.0	0.09	401	11.2	0.03	17	210	19
	4-cycle	89	6.9	0.9	0.09	104	3.5	0.03	20	119	13

* Rated speed for each test is about 50 mph mean road speed. This is probably the engine condition producing maximum mass emissions, including smoke.

of 13 to 210 in Table B-4 for diesels. This data roughly implies that diesels are probably more significant source of NO_x than gasoline-powered vehicles.

7. An additional point concerning nitrogen oxides is that with diesels 15 to 60 percent of the nitrogen oxides are present as nitrogen dioxide; with gasoline engines the nitrogen dioxide is less than about 10 percent. This has been attributed (1) to the higher compression ratio of diesels as compared to gasoline engines and the higher concentration of oxygen present during combustion.

8. In contrast to the above, diesels produce several other pollutants in much larger quantities than gasoline-powered vehicles; these are smoke and irritating and odorous compounds. These will be discussed later.

D. Gasoline-vehicle evaporative losses. These, of course, are almost entirely hydrocarbons of the types contained in the gasoline blend being used for fuel.

E. Summary. In relation to these data, it may be concluded that diesels are not a major source of community-wide air pollution, being few in number compared to gasoline-powered vehicles, being in general more efficient combustors of fuel, and having comparatively low crankcase emissions and evaporative losses. Problems associated with diesels are generally local in nature, i.e., smoke and odor.

V. Specific pollutant types. Interest in hydrocarbon pollutants is concerned not only with the general aspects discussed up to this point but also to specific pollutants related to specific effects. This emphasis has come about for various reasons: (1) the realization, as our research knowledge grows, that all effects are not caused by a single pollutant, nor even a single class of pollutants: (2) the realization that control on a "general basis may not necessarily alleviate all effects or any one specific effect, and (3) control methods aimed at specific pollutants might attain the same aims sooner and at less cost. For these reasons, it is worthwhile to examine available detailed knowledge of vehicle pollutant emissions; the individual hydrocarbon compounds present in automotive emissions are quite important in relation to the degree they participate in photochemical smog reactions.

A. Gasoline-vehicle tailpipe emissions. The following facts are important in the consideration of detailed components in gasoline-vehicle exhaust.

1. Some 50 or more individual hydrocarbons have been identified to date in the exhaust gases. Most of these, with few exceptions, are found for all fuels and all modes of engine operation. These include: Acetylenes, mono-olefins with both terminal and internal bonding in the C_2-C_5 range, diolefins, straight-chain paraffins, branched-chained paraffins, cycloparaffins, and aromatics.

2. Identification to date has been principally for the lower molecular weight species, i.e., C_1C_6 paraffins, C_2-C_6 olefins, and C_6-C_9 aromatics. Work is underway to extend these analysis to the higher molecular weight hydrocarbons.

3. Two factors exert a significant influence on exhaust composition: (1) engine variables, and (2) fuel composition.

4. Fuel composition heavily influences exhaust composition during idle and deceleration.

5. For steady-state conditions under high engine-load demand, such as cruise, all fuels indicate a general trend toward 2- through 4-carbon olefins and decreasing paraffins-naphthenes. This is not observed for 5-carbon and heavier olefins.

6. Aromatic content is essentially constant for all modes of engine operation.

7. All fuels, including those of low olefin content, produce significant amounts of exhaust olefins. Heavier olefins with 4 or more carbon atoms, reflect the olefin content of the fuel. The 2- and 3-carbon olefins account for 40-90 percent by weight of mono-olefins present.

8. High alkylate (paraffin-naphthene) fuels produce olefins approximating those produced by fuels containing 40-50 percent olefins.

9. Fuels of aromatic content produce lower but significant quantities of olefins. All fuels, except the low aromatic saturated type, produce significant quantities of xylene and benzene in the exhaust.

10. Aromatic content of the exhaust reflects directly the aromatic content of the fuel.

11. Significant quantities of C_1 through C_5 paraffins are produced.

12. Although it is hazardous to attempt to summarize constituents in auto exhaust covering the gamut of all fuels and driving conditions, the data in Table B-5 reflect current knowledge. The particular breakdown shown has been purposely selected in relation to photochemical reactivity, which will be discussed later.

Table B-5

RELATIVE ABUNDANCE OF VARIOUS HYDROCARBONS IN AUTO EXHAUST

Hydrocarbon Class	Relative Abundance (Light, Medium or Heavy)
C_1-C_5 paraffins	Heavy
C_6 and higher paraffins	Heavy
C_2-C_4 olefins	Heavy
C_5 and higher olefins	Medium
Diolefins	Light
Acetylenics	Medium
Benzene	Medium
Toluene	Heavy
Xylenes	Heavy
C_9 and higher aromatics	Medium

B. Gasoline-vehicle crankcase emissions

1. As stated previously, these emissions reflect to a large extent the constituents contained in the gasoline blend used for fuel.

2. Practically all petroleum hydrocarbons found in gasoline are members of four major groups: paraffins and napthenes (cycloparaffins, olefins, and aromatics.

3. Classification of groups by increasing knock values is as follows: Straight-chain paraffins, branch-chain paraffins, olefins, napthenes, and aromatics.

4. California gasolines have larger proportions of naphthenic and aromatic compounds than those from eastern fields, which are largely paraffinic. However, various refining processes are now used to produce gasolines of better antiknock characteristics. Table B-6 indicates the gasoline constituents obtained from these processes (6).

Table B-6

HYDROCARBON TYPE OBTAINED FROM DIFFERENT REFINING PROCESSES

Process	Paraffins and Naphthenes (%)	Olefins %	Aromatics %
Straight-run	98-100	1	1
Thermally cracked	50	25	25
Catalytically cracked	40	40	20
Catalytically reformed	54	1	45
Alkylation	100	0	0

5. Crankcase emissions for the most part reflect these fuel characteristics and to a much lesser extent exhaust products. As previously discussed, the contribution of engine oil characteristics to crankcase ventilation composition is as yet undetermined.

C. Gasoline-vehicle evaporation losses.

1. Since these losses directly reflect the composition of the fuel, their significance can be assessed by knowledge of detailed hydrocarbon composition of the fuel as indicated above for crankcase emissions.

D. Diesel-vehicle tailpipe emissions.

1. Hydrocarbon emissions.

a. Because hydrocarbon emissions from diesels already meet the gasoline vehicle standards of 275 ppm, only limited studies have been made concerning a detailed breakdown of individual constituents.

b. These limited studies indicate that exhaust components reflect fuel composition. However, a full complement of lower-molecular-weight hydrocarbons, including methane, ethylene, acetylene and other C_2-C_5 paraffins and olefins have been identified.

c. The role of diesel exhaust in photochemical smog is essentially unexplored. Additional work in this area, as well as sources of hydrocarbon other than automotive vehicles, is needed to better define the potential of these sources to photochemical smog.

2. Smoke emissions.

a. The importance of diesels in the pollution problem stems from production of compounds producing local nuisance effects: smoke, and irritating and odorous compounds.

b. Diesel smoke has been generally classified into several types (1) "Hot" smoke, generally black, consists of solid carbonaceous particles and occurs during warm engine operation load conditions as the stoichiometric air-fuel ratio is approached. Such soot results from locally overrich mixtures in the combustion chamber.

c. "Cold" smoke, generally described as light or white, is principally unburned or partly oxidized liquid particles of fuel or lubricating oil resulting from quenched combustion, especially at idle or at light load where air-fuel ratio is high. Emissions of cold smoke are aggravated by intensive mixing of small fuel quantities at light load with cold air, or by contact of the fuel with cold chamber walls.

d. "Blue" smoke, which does not become visible until several feet from the exhaust outlet, is heaviest under medium load. It probably consists of condensed hydrocarbons.

e. Maximum rated loads for diesels are based on an air-fuel ratio giving a moderately smoky exhaust. Lugging of the engine by the operator, either because of improper training, e.g., overloading rather than gear shifting, or because of inherent deficiencies in the transmission system, aggravates hot smoke emissions. Lugging is defined as any operating condition where the engine speed decreases or does not increase either under full throttle conditions or when the throttle is opened further. Because of its superior lugging ability, the diesel truck engine is generally operated at lugging conditions 2 to 4 times that of the gasoline engine, by failure to shift to a lower gear ratio for the particular road and traffic conditions encountered.

f. Obvious cure for hot smoke is operation at engine loading within manufacturer's specifications, and maintenance of engine auxiliary equipment (air filters and fuel injection system) to give proper air-fuel ratios. Derating the engine, as a means to reduce the inadvertant occurrence of lugging conditions, would be beneficial in reducing smoke emissions. Manufacturers rate diesel engines at present on the basis that they shall be capable of operation between maximum torque and full rated power for all engine speeds without producing smoke in excess of No. 2 Ringleman in the exhaust. A No. 1 specification would, then, result in reduced smoke emissions at the expense of providing a larger engine for the anticipated use.

g. Proper fuels are a requisite for the control of at least some types of smoke. Black smoke appears to be little affected by fuel quality, providing,of course, manufacturer's specifications are met. In contrast, blue smoke, which is heaviest under medium load conditions, appears to be affected by certain components in the diesel fuel. To date the smoke-producing components have not been specifically identified, but appear to be related to both fuel volatility and composition.

h. Engine acceleration also affects the total smoke level. Generally acceleration produces more smoke for a short period of time than is produced under the power equilibrium conditions.

i. Recently additives to diesel fuel have been developed (one of these, Lubrisol, is a fuel soluble barium compound) which effect a reduction of smoke. It has been field tested in Europe and found to be generally beneficial in reducing smoke. Possible adverse effects on engine maintenance have not been fully explored. Cost of the additive is about 1-1/2 to 2 cents per gallon compared to diesel fuel cost of 22 cents per gallon. One problem concerned with the use of such additives is that truck operators may still lug their engines sufficiently to produce smoke in spite of regulations requiring their use. Hence their full effectiveness can be offset by improper truck operations. Also possible toxic effects of barium compounds discharged to the atmosphere have not as yet been clearly defined.

j. It is generally agreed that proper maintenance and fuel selection, operator training, derating of engines, proper transmissions, and avoidance of overloading and prolonged idling will satisfactorily prevent smoke. Hence the problem is one more of effective regulation and enforcement than lack of technology. The complications of effective regulations and enforcement, however, are so great as to be impracticable. What is needed is a method which is simple and one which still cannot be compromised by the operator, e.g., a tailpipe device which will remove smoke.

3. Irritant and odorous emissions.

a. These components include those that are irritants to the eyes, nose, throat, and chest, and those that produce nausea.

b. No physical or chemical evaluation methods are available, since the relationship between the multitude of constituents and subjective response have not been established.

c. Aldehydes (including arcrolein) have been singled out for attention, as these have been found in diesel exhaust. These compounds have been found in similar concentrations in auto exhaust, and hence the case against them is far from complete.

d. The identification of other oxygenated compounds is largely unexplored, as is the contribution of nitrogen dioxide and smoke and particulate matter to the odor and irritant qualities of diesel exhaust. Other types of compounds which have received some attention are organic acids and ketones.

e. Generally odor intensity follows the trends for black smoke indicating a minimum level at the mid-power engine condition, increasing as the power output of the engine approaches full rated power. This trend differs, however, in that for some engines there is an increase in odor intensity as power is reduced from the mid-range to low power conditions such as idle, deceleration, or acceleration after idle. This increase may be attributed to chilling of the combustion chamber and reacting substances with the great excess of air.

f. Production of odorous and irritant compounds may be controlled to a degree by the same methods used to control smoke, but this is not the whole answer. Methods suggested specifically for control of odor are use of catalytic mufflers, use of low-sulfur-content fuels, use of masking agents, and possible reduction of air-fuel ratio at light loads. The full efficacy of these is yet to be determined. There is on the market at present a number of catalytic devices that appear to be effective for odor control. Although the odor threshold is not changed, subjective evaluation of odor response indicates there is an improvement in odor quality, in that the modified exhaust is more acceptable and loses its typical diesel odor characteristics. Some reduction in hydrocarbon is also affected.

4. California standards for vehicle smoke and odor emissions.

The California Department of Public Health, in September 1963, adopted a standard for smoke emitted from a motor vehicle (including diesels). This standard limits the shade, or the equivalent opacity of the shade, to that designated as No. 1 on the Ringleman Chart or to that designated as Ringleman No. 2, if the smoke is for a period not exceeding 5 seconds at a time. An odor standard was set by California in June 1966. At the present time the Motor Vehicle Pollution Control Board is establishing test criteria for the certification of control methods.

Perhaps the greatest roadblock to the setting of odor standards for diesels is the availability of an objective reproducible odor standard. The California standard specifies a panel for rating odor objectionableness. The Federal government is attempting to develop and utilize odor kits for odor quality and intensity evaluations, so that panels all over the country and under varying climatic conditions will have standard benchmarks for odor evaluation. The use of the kits by panels will of course have to be compared with the judgement of a large number of people in order to relate the kits to public opinion. Hopefully, also, a chemical method may be developed, which would relate, say, a series of chemical compounds to odor objectionableness. The merits of eliminating the need for expensive panels is obvious.

VI. In-traffic carbon monoxide levels.

A. It has been suggested that occupants of passenger cars operating under heavy traffic conditions, or individual whose employment requires them to be on the city streets for extended periods (e.g., traffic police and highway repair crews), are subject to unusually heavy exposure to carbon monoxide. It has been suggested that such exposures may account in some part for driver fatigue and be a contributing factor in highway accidents.

B. Although environmental CO levels are routinely measured in a number of cities, the monitoring sites do not reflect the exposure of humans engaged in activities near ground level on the streets. Samples taken inside of moving vehicles or immediately adjacent to the highway indicate levels several times those measured at sites set back somewhat from the highway. For example (7), a series of tests involving the Continuous Air Monitoring Program stations indicated that the median of 30 minutes average samples collected inside vehicles in traffic exceeded 5 minute average samples at the Continuous Air Monitoring Program station collected during the same period by 1.1 to 6.7 times, depending on the set-back of the Continuous Air Monitoring Program station from the street.

C. Additional studies are now under way involving a mobile unit equipped to sample continuously inside vehicles for CO and hydrocarbons. These studies are being conducted in a number of cities and are investigating various moderate to heavy traffic conditions heavily traveled, wide expressways, main city streets with moderately rapid traffic, and center city streets with slow moving traffic. In traffic CO values in all cities sampled exceed 30 ppm in at least 10% of the 30-minute

integrated samples. The range of city averages was 21-39 ppm carbon monoxide and the range of integrated samples was 7-77 ppm carbon monoxide. Generally it was found, as one might expect, that high concentrations result from a combination of high levels of source emissions and limited ventilation, eg., in downtown canyons, depressed freeways hemmed in by structures, etc.

VII. Particulate emissions from vehicles.

Although emphasis to date has not been given to the role of vehicle particulate emissions to the total particulate burden of community atmospheres, it should be noted that their contribution is not in any sense a minor portion of the total, especially where stationary sources have been brought under control. Table A-4 indicates that daily aerosol emissions from vehicles in 1965 in Los Angeles County amount to 47 tons per day compared to a total from all sources of 115 tons per day in summer and 140 tons per day in winter, or 41% in summer to 34% in winter. In 1970 the vehicular contribution is estimated to be 55 tons per day and will account for 48% in summer to 31% in winter (9). Table A-7 indicates a substantial range in the aerosol contribution to the total in eleven Pennsylvania counties.

Also to be noted is that the vehicular contribution of aerosols consists of those emitted directly (smoke and the combustion products of gasoline additives, e.g., lead alkyls) and those formed in the photochemical oxidation process. Only little attention to development of control methods for vehicular particulate emissions (except for diesels) has been given to this area to date. Logically it will be included for future investigation and control.

VIII. California standards for nitrogen oxides emissions from vehicles.

The California State Board of Public Health on October 29, 1965 adopted NOx standards for both ambient air quality and motor vehicle exhaust emissions. The standard for air quality was set for nitrogen dioxide at 0.25 ppm for one hour at the adverse level, (based on atmospheric coloration and visibility considerations), and 3.0 ppm for one hour for health effects. The standard for motor vehicle emissions, based on 65% reduction of all sources, both vehicular and stationary, required to maintain the 0.25 ppm level for one hour in Los Angeles in 1980, was set at 350 ppm. The nitrogen oxide emission of vehicles varies from about 870 ppm for cars with manual transmission to 1075 ppm for cars with automatic transmission to give a weighted average of 1000 ppm (10). Test procedures for certifying devices for nitrogen oxides control were adopted on August 10, 1966. No devices have been received by the MVPCB for certification as yet.

It is stressed that this standard is based on 65% from all vehicular sources, including diesels, and all stationary sources. Further it is noted that the standards are not based on photochemical smog effects, it being held that the major control of smog will result from control of hydrocarbons alone, and that nitrogen oxides control would be effective only if ambient air standards were set at 0.1 ppm or less.

As with hydrocarbon and carbon monoxide control standards for vehicles, control devices will be required only after two or more devices have been certified by the California Motor Vehicle Pollution Control Board.

IX. Summary for Section B.

In the discussion so far an attempt has been made to establish the relative contributions of classes of pollutants from various types of gasoline- and diesel-fueled vehicles. The smoke and odor from diesels constitutes a local nuisance problem of some magnitude; methods for both defining and controlling the latter are not known and are being investigated. Levels of hydrocarbon, nitrogen oxides, and carbon monoxide have been established for gasoline engine exhaust, crankcase ventilation and evaporation losses, and diesel exhausts. An attempt has been made to assess specific hydrocarbon constituents in these various sources, in that it forms the background to discuss photochemical reactions involving vehicle emissions to the atmosphere.

References (Section B)

1. Kinosian , J. R. et al., The Diesel Vehicle and Its Role in Air Pollution, A Report to the California Legislature, State of California, Department of Public Health, Berkeley, California, December 1962.

2. Brubacker, M. L., Role of Trucks and Buses in the Air Pollution Problem, State of California, Motor Vehicle Pollution Control Board, Los Angeles, California, February 14, 1962.

3. The Auto Smog Story, 1964 Biennial Report, California Motor Vehicle Pollution Control Board, January 1965.

4. Unpublished data, U. S. Public Health Service, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio.

5. Rose, A. H., Jr., et al., Comparison of Auto Exhaust Emissions from Two Major Cities, JAPCA, 15:362-366, August 1965.

6. Motor Vehicles, Air Pollution and Health, U. S. Department of Health, Education, and Welfare, Washington, D.C., June 1962.

7. Automotive Air Pollution III, Report of the Secretary of the Department of Health, Education, and Welfare to the U. S. Congress, December 1965.

8. Brice, R. M. and Roesler, J. F., The Exposure to Carbon Monoxide of Occupants of Vehicles Moving in Heavy Traffic, JAPCA, 16:597-600, November 1966.

9. Report of the Scientific and Emergency Action Committee, Los Angeles County Air Pollution Control District, Los Angeles, California, January 13, 1965.

10. The Oxides of Nitrogen in Air Pollution, State of California, Department of Public Health, Berkeley, California, July 15, 1965.

11. Clarke, P. M., et al., An Adsorption-Regeneration Approach to the Problem of Evaporative Control, Paper No. 670-127, SAE Automotive Engineering Congress, Detroit, Michigan, January 13, 1967.

Section C

Photochemical Reactions in the Atmosphere

(Outline)

I. General Considerations

- A. Source and meteorological factors
- B. Types of photochemical reactions

II. Primary Photochemical Processes

- A. Nitrogen dioxide
- B. Conversion of nitric oxide to nitrogen dioxide
- C. Formation of ozone
- D. Organic reactions
  1. Atomic oxygen reactions
  2. Ozone reactions
  3. Nitrogen oxide reactions
  4. Nitrogen oxide - sulfur dioxide reactions
- E. Effect of concentration, relative abundance and nature of reactants
  1. Concentration
  2. Relative abundance
  3. Nature of reactants
  4. Other considerations

C. PHOTOCHEMICAL REACTIONS IN THE ATMOSPHERE

I. General considerations

A. Source and meteorological factors. The reactions that take place in the atmosphere depend both on the variations of the source and on meteorological factors.

1. Source variation. The production of automobile exhaust varies, of course, with traffic density, which depends upon the habits of the residents, particularly with respect to the normal working period. We would expect, therefore, a peaking of sources in the morning (7:30 to 9:30 a.m.) and in the late afternoon (4:00 to 6:00 p.m.) corresponding to the traffic build-up going to and returning from work.

2. Meteorological factors. Meteorology plays a major role in the production of photochemical smog in that it dictates the dilution of the source materials and the intensity and duration of solar energy available to the photochemical process. Major factors are:

a. Inversions. Frequency, duration and height. Inversions not only control the extent of daily vertical mixing, but their duration over periods of several days results in build-up of pollutants with time.

b. Wind. Wind, or the lack of it, and its fluctuation with time control (a) the areal (both lateral and longitudinal) distribution or dilution of pollutants, and (b) the relationship of the partially photolysed air parcel to replenishment of unreacted fresh source materials.

c. Solar radiation. The intensity, variation, and duration of solar radiation controls the input of ultraviolet light required to initiate and extend the photochemical process. The region from 2900 A, the lower solar cutoff, to 4000 A° is of particular interest in relation to photochemical smog. Hence shielding by clouds, the extent of daylight hours, i.e., seasonal effects, the over-all cleanliness of the air related to solar absorption and scattering, radiation from the sky and reflection from the earth are all important factors in the photochemical process. It is noted that the "smog" season in California is in the fall when neither solar radiation nor frequency of low inversions are highest, but rather the optimum combination of the two. It is fortunate, indeed, that these do not both occur in the summer period.

d. Experimental simulation. Research studies relative to photochemical smog cannot, of course, afford the randomness of all of these variables. Concentrations of pollutants and intensity and duration of irradiation are relatively easily handled. Variations of solar energy by time of day and the carry-over of smog from one day to the next have not been investigated, but only because these are considered to be "less important" variables. The problem of replenishment of

the reacting smog parcel with raw and therefore unreacted exhaust has been investigated at the two extremities of the spectrum; (a) by static systems wherein a parcel of polluted air is irradiated with no incoming raw pollutants, and (b) by dynamic or stirred reactor systems wherein raw pollutants are added to the system and irradiated contents withdrawn in a like amount on a continuous basis.

B. Types of photochemical reactions. Photochemical reactions can be divided into several classes. Although the principal one believed to be involved is the first on the list (homogeneous reactions), the others are included to indicate the complexity of the situation in relation to (a) our knowledge as determined by research accomplished to date, (b) the role these factors may play in physical and biological effects, and (c) the complications involved in possible control methods.

1. Reactions between gaseous species, i.e., homogeneous gas reactions.

2. Reactions between gaseous species on catalytic surfaces, i.e., heterogeneous gas reactions.

3. Adsorption of gases on the surfaces of particles (important in effects aspects).

4. Reactions of gases with chemical species present on particle surfaces.

5. Reactions initiated on photochemically activated surfaces.

6. Liquid-phase reactions as gases dissolved in liquid aerosols.

II. Primary photochemical processes (1)

A. Nitrogen dioxide. Nitrogen dioxide appears to be of primary importance as an initiator of photochemical reactions, although other substances (SO_2, alkyl nitrites, ozone, and aledehydes) may be of minor significance. Nitrogen dicxide is dissociated between 2900 and 3700° as follows:

$$NO_2 + h_\nu \rightarrow NO + O \qquad (1)$$

B. Conversion of nitric oxide to nitrogen dioxide.

1. Since most nitrogen oxides from vehicles are emitted as nitric oxide, a mechanism involving other species must take place in the atmosphere in converting the NO to NO_2, in that conversion by atmospheric oxygen alone is much too slow by several orders of magnitude in relation to what has been observed in the atmosphere or under controlled experimental conditions.

2. It appears that a free-radical chain reaction is the mechanism responsible for this conversion, and that the other species involved are princically hydrocarbons (although other organics such as alde-

hydes can assist in this conversion. This chain is assumed to start with the formation of atomic oxygen as indicated in reaction (1).

$RH + O \rightarrow R + OH$; Formation of alkyl radical (R) from organic (RH) (2)

$R + O_2 \rightarrow RO_2$; Formation of peroxyl alkyl radicals (RO_2) (3)

$RO_2 + NO \rightarrow RO + NO_2$ (4)

C. Formation of ozone.

1. Only after almost all of the NO has been converted to NO_2, does ozone appear in appreciable quantities (note Fig. C-1).

2. Usually the ozone does not reach its maximum value until well after the NO_2 peaks and begins to decrease.

3. Formation of ozone is postulated to result from a number of reactions, the principal ones being:

$$NO_2 + h_\nu \rightarrow NO + O \quad (1)$$

$$O + O_2 + M \rightarrow O_3 + M \quad (5)$$

4. Ozone is consumed to a small extent by photo-decomposition and thermal decomposition, and by means of the following reactions:

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (7)$$

$$RH \text{ (hydrocarbons)} + O_3 \rightarrow \text{Products} \quad (8)$$

5. Reactions (1), (5), and (7) are of importance in determining the quantity of the ozone present. However, in the absence of (8), the ozone concentration maintained is negligible. Hence reactive organice compounds as outlined earlier are necessary to keep the chain going, as well as to convert the NO to NO_2 initially.

6. The mechanism by which organic species participate has not been established. As discussed previously, reactions (2), (3), (4) and (8) have been suggested, but this simplification leaves a number of questions to be answered, particularly in reference to the less reactive hydrocarbons.

D. Organic reactions. These have been discussed previously in relation to the conversion of NO to NO_2 and in the production of ozone and atomic oxygen. Also involved are the formation of products containing nitrogen and sulfur, the latter being of particular significance in relation to production of aerosols.

1. Atomic oxygen reactons. The most reactive species in olefins, probably the only reaction of importance. Very little splitting of the double bond takes place, and the products formed are epoxides, aldehydes, or ketones with the same number of carbon atoms as the olefin. Reaction rates are quite low, and cannot account for overall disappearance of olefins. Rates for other hydrocarbons species are 1 to 3 orders of magnitude less.

2. Ozone reactions. Reactions with ozone probably account for a very significant portion of the total reactivity of organic species in the atmosphere, since the rates for olefins are some 10 to 100 times those involving atomic oxygen. Olefin species are split at the double bond with the formation of an aldehyde or ketone plus other products (a zwitter ion) which decompose in gas phase reactions to form products including paraffins, olefins, formic acid, methanol, ketone, CO, CO_2, and water. Data on ozone reactions for other compounds are not too abundant, and more data are needed for species such as aromatic hydrocarbons and aldehydes.

3. Nitrogen oxide reactions.

a. In addition to their role in the chain process of photochemical smog, nitrogen oxides combine with the organics to form products (Equation (8) and Fig. C-1).

b. Olefins have been shown to produce a class of compounds called peroxyacylnitrates: $(RCO)OONO_2$

c. The first two homologues in the series are peroxy (acetyl) nitrate (PAN): $(CH_3CO)OONO_2$; and peroxy (propionyl) nitrate (PPN): $(CH_3CH_2CO)OONO_2$

d. PAN can be formed from the olefin trans-2-butene and PPN from 1-pentene or 1-hexene.

e. Minor compounds formed include alkyl nitrates, epoxides, methanol, formic acid, and aldehydes.

f. The peroxycacylnitrates are known to be both phytotoxicants as well as lachrymators.

4. Nitrogen oxide - sulfur dioxide reactions. The irradiation of NO_x-SO_2-organic system results in the production of aerosol, which is reponsible for a good share of the haze and reduction of visibility in Los Angeles. One suggested mechanism is that during the processes in volving the reactive organics previously outlined, the SO_2 is oxidized to SO_3, which is then converted to H_2SO_4 mist by combining with the water vapor in the air.

E. Effect of concentration, relative abundance, and nature of reactants.

1. Concentration. Complex photochemical reactions involving NO_x and organic compounds are concentration-dependent relative both to rates and equilibrium concentrations of products. For example ten-fold increases in reactant concentration results in only small increases in oxidant production. This factor must then be considered in the interpretation of experimental and environmental data.

2. Relative abundance.

a. The relative abundance of the primary reactants, i.e., the HC/NO_x ratio, influences the products formed.

b. This latter point has been of great interest the last several years in California, and stems from arguments by proponents of various theories as to whether control of hydrocarbons without simultaneous control of NO_x (as is now contained in the California law and in Federal regulations for 1968 model-year passenger cars) will result in more rather than fewer deleterious effects.

c. It is postulated that reduction of organics without reduction in nitrogen oxides will result in higher levels of NO_2, which is a toxicant itself and which will result in further reduction in visibility by production of a "whiskey" colored atmosphere due to the color of NO_2.

3. Nature of reactants.

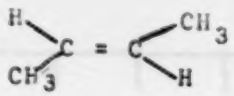
a. Hydrocarbons as a class (and a few organic species contained in vehicle exhaust) must be further subdivided on the basis of their "reactivity" or ability to participate in photochemical reactions. Several arbitrary methods of rating "reactivities" have been proposed, e.g., a) conversion of NO to NO_2, b) oxidant production, c) hydrocarbon consumption, and d) effects produced such as eye irritation or plant damage. Since the degree of objectionableness of a species is more a function of effects produced during irradiation over a day's period, the latter three measures are considered to be more realistic than the first, i.e., NO to NO_2 conversion rate. Table C-1 is a listing on the basis of hydrocarbon consumed near dynamic equilibrium conditions. (A comprehensive discussion of this subject is given in Reference (2).

b. The conversion of NO to NO_2 in photochemical smog is typified by Fig. C-1, representing and irradiation run in a dynamic chamber. Results from irradiation in a static chamber are similar. Note that a) the initial conversion of NO to NO_2 occurs within the first 50 minutes or so after the initiation of irradiation, b) NO_2 peaks when NO has been essentially eliminated, c) oxidant production and hydrocarbon consumption becomes substantial only after the NO has been converted to NO_2, and d) the NO_x is converted to products as well as the hydrocarbons.

c. Actual photochemical smog occurrences similar to that shown in Fig. c-1 are quite common for locations in California. An example from Philadelphia is shown in Fig. C-2 (3). Note the similarity to Fig. C-1, e.g., conversion of NO to NO_2, the production of oxidant, and decrease in hydrocarbons.

Group 1:

Internally double bonded olefins such as

Trans-2-butene: 

Group 2:

Alkenes (externally double-bonded olefins) such as

Butadiene: $H_2C = CH - CH = CH_2$

Butene : $CH_3 - CH_2 - CH = CH_2$

Propylene: $CH_3 - CH = CH_2$

Aromatics such as

Trimethyl benzenes: 1,3,5- and 1,2,4-

Group 3:

Ethylene (2 carbon olefins): $H_2C = CH_2$

Dimethyl benzenes or xylenes (aromatics): 1,2- and 1,4-

Aldehydes: formaldehyde (HCHO) and propionaldehyde (CH_3-CH_2- CHO)

Group 4:

Methlyl benzene or toluene: $CH_3-C_6H_5$

C_6 and higher paraffins (saturates)

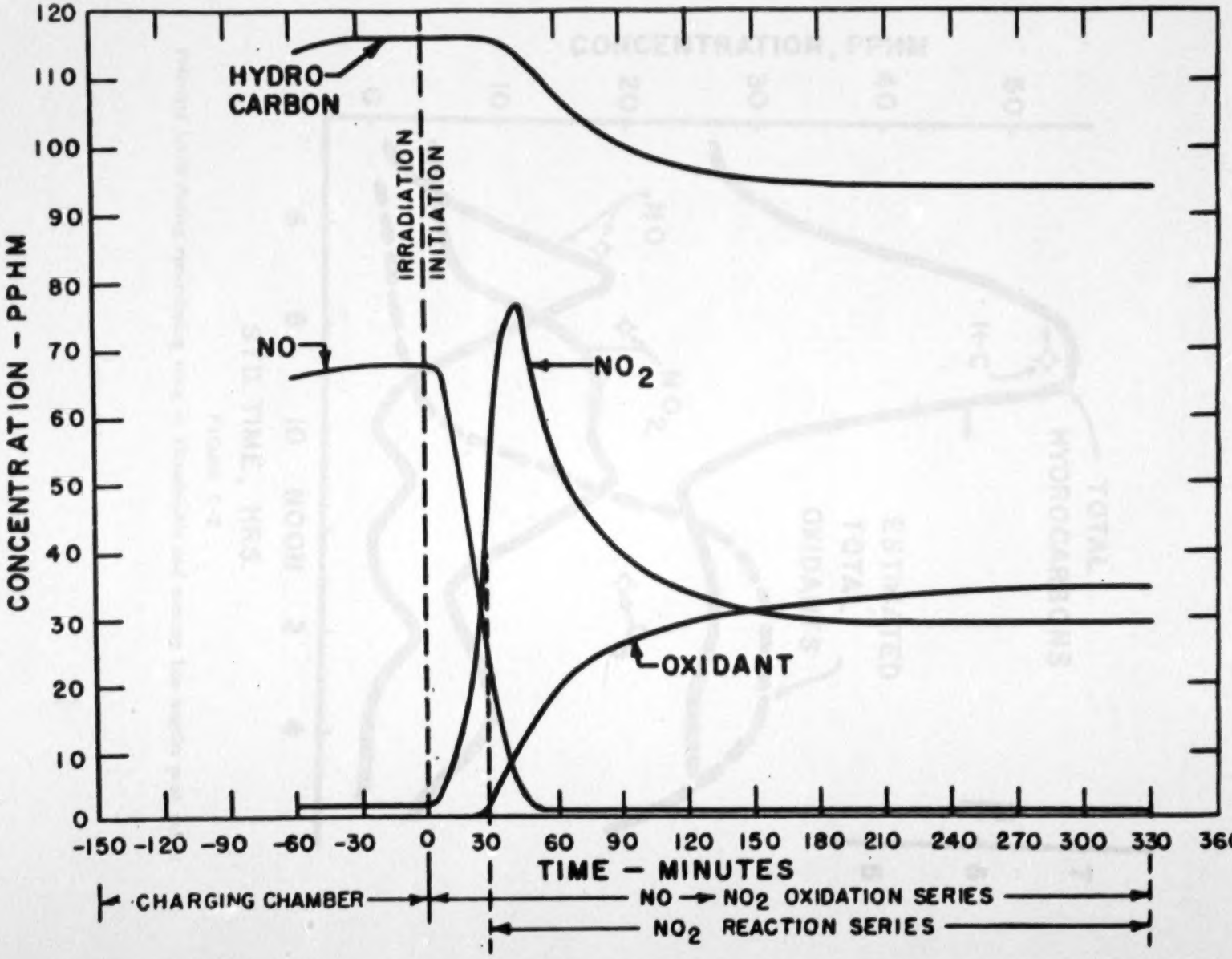
Acrolein: $CH_2= CH - CHO$

Group 5:

C_1-C_5 paraffins (saturates)

Acetylene: $HC = CH$

Benzene: C_6H_6



CHEMICAL RELATIONSHIPS FOR A TYPICAL CHAMBER REACTION

FIGURE C-1

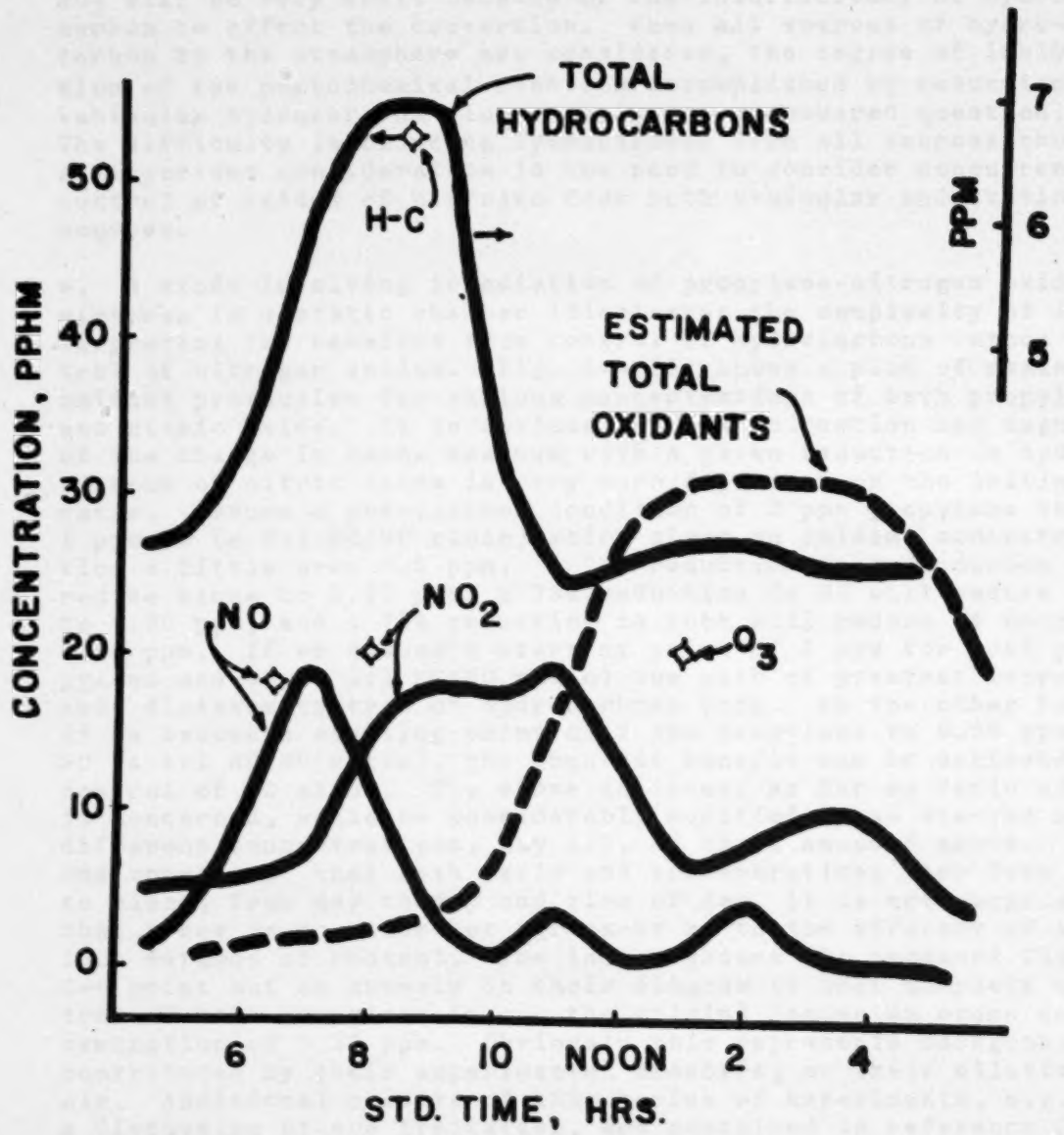


FIGURE C-2

Pollutant levels during eye-irritating smog in Philadelphia and average Los Angeles peak values

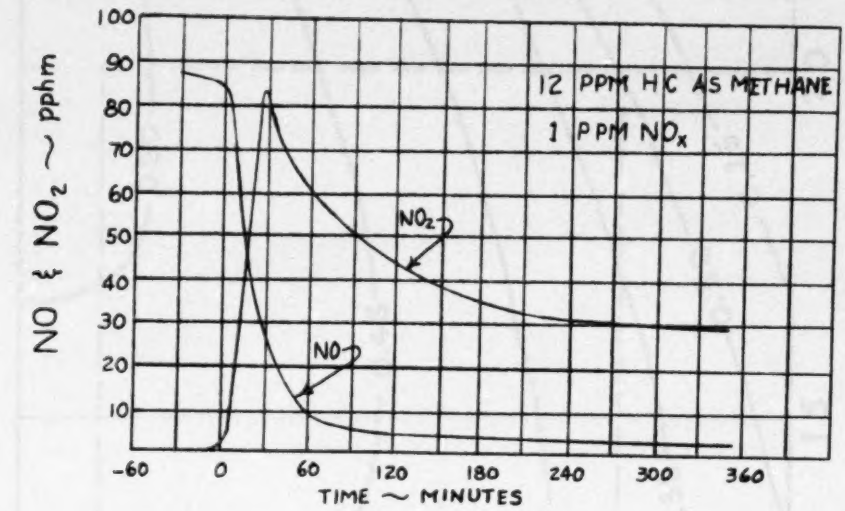
d. Results of a series of tests by the Public Health Service (4) for various HC/NO_x ratios at concentrations of hydrocarbon ranging from existing smoggy-day levels to those obtained under the California standards (80 percent reduction) is shown in Fig. C-3. Note that unreacted NO_2 increases from 30 pphm for a ratio of HC/NO_x of 12 to 1, to 60 pphm for a ratio of 3 to 1. (Note that hydrocarbon is expressed as ppm of methane.) As hydrocarbon is further decreased, the amount of NO converted to NO_2 will be very small because of the insufficiency of hydrocarbon to effect the conversion. When all sources of hydrocarbon to the atmosphere are considered, the degree of inhibition of the photochemical reaction accomplished by reduction of vehicular hydrocarbons alone remains an unanswered question. The difficulty in reducing hydrocarbons from all sources thus is an important consideration in the need to consider concurrent control of oxides of nitrogen from both vehicular and stationary sources.

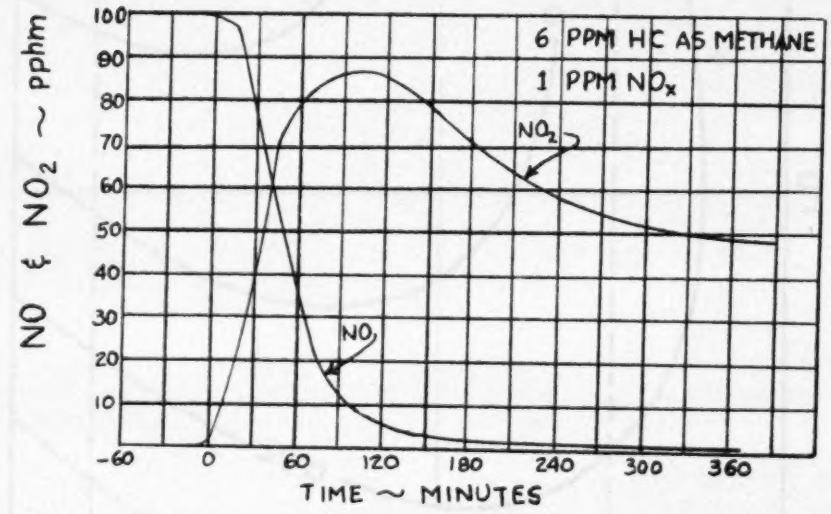
e. A study involving irradiation of propylene-nitrogen oxide mixtures in a static chamber illustrates the complexity of interpreting the benefits from control of hydrocarbons versus control of nitrogen oxides. Fig. C-4 (5) shows a plot of maximum oxidant production for various concentrations of both propylene and nitric oxide. It is obvious that the direction and magnitude of the change in ozone maximum with a given reduction in hydrocarbons of nitric oxide is very much dependent on the initial ratio. Assume a pre-control condition of 2 ppm propylene to 1 ppm NO (a 2:1 HC/NO ratio) which gives an oxidant concentration a little over 0.5 ppm. A 75% reduction in hydrocarbon will reduce ozone to 0.27 ppm; a 75% reduction in NO will reduce ozone to 0.30 ppm, and a 75% reduction in both will reduce it only to 0.33 ppm. If we assume a starting point of 1 ppm for both propylene and NO (a 1:1 HC/NO ratio) the path of greatest improvement dictates control of hydrocarbons only. On the other hand, if we assume a starting point of 2 ppm propylene to 0.50 ppm of NO (a 4:1 HC/NO ratio), the greatest benefit can be achieved by control of NO alone. The above analyses, as far as ratio alone is concerned, would be considerably modified if we started at different concentrations, say 1/2, of those assumed above. When one considers that both ratio and concentrations vary from place to place, from day to day and time of day, it is not surprising that there is no clear-cut agreement as to the efficacy of various methods of control. The investigators who produced Fig. C-4 point out an anomaly in their diagram in that complete control of both propylene (e.g., the origin) leaves an ozone concentration of 0.23 ppm. Obviously this represents background contributed by their experimental chambers, or their dilution air. Additional results of this series of experiments, e.g., a discussion of eye irritation, are contained in reference C-6.

4. Other considerations.

a. Ad indicated previously, the nature of the hydrocarbons and other organics relative to the reactivity is very important in photochemical smog production. Implications relative to control are very important, particularly in reference to practicable methods at reasonable cost.

NO & NO_2 CHAMBER REACTIONS





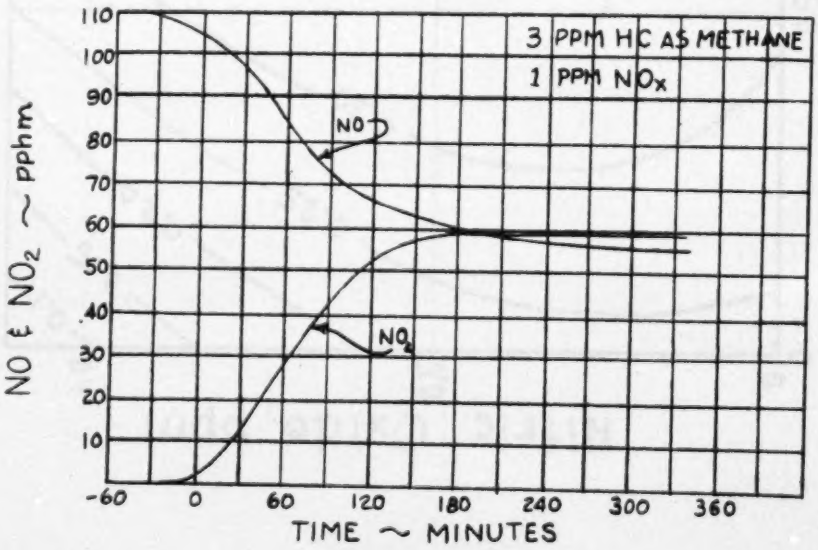


FIGURE C-3

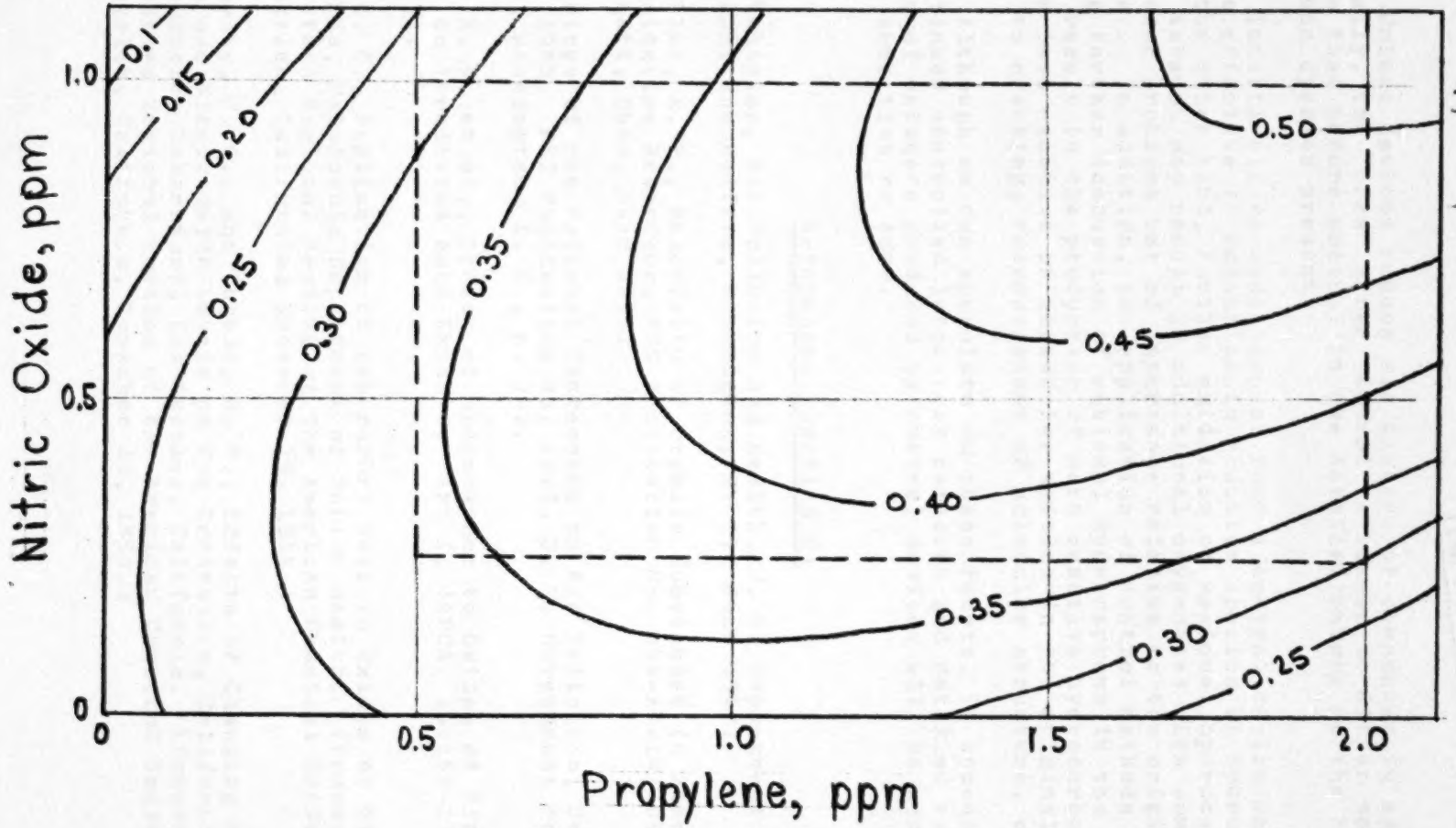


Figure C-4. Oxidant Maxima in ppm for Various Concentrations of Propylene and Nitric Oxide (Reference C-6).

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b. Unless devices reduce all classes of compounds in exhaust equally, the "brew" after control is likely to differ markedly from that before control in the detailed nature of the hydrocarbon species present.

c. Intuitively we would expect that a control device would be more effective in reduction in reactive species of hydrocarbon. On the other hand, further oxidation of residual hydrocarbons in the exhaust may result in additional oxygenates with some chance of odor problems not of importance relative to the original exhaust. In addition, the application of control methods involving further combustion of residual hydrocarbons in the exhaust may result in the production of more reactive hydrocarbon species from less reactive or unreactive species in the original exhaust due to cracking, rearrangement of molecular structure, etc.

d. Although we can speculate on these facets, it appears that continued controlled laboratory research and detailed examination of exhausts produced by control devices will be necessary for some time to come.

References (Section C)

1. Motor Vehicles, Air Pollution and Health, U. S. Department of Health, Education, and Welfare, Washington, D. C. June 1962.

2. Altshuller, A. P., Reactivity of Organic Substances in Atmospheric Photooxidation Reactions, PHS Publication No. 999-AP-14, USDHEW, Cincinnati, Ohio, July 1965.

3. Proceedings of the National Conference on Air Pollution, December 10-12, 1962. PHS Publication No. 1022, U. S. Government Printing Office, Washington, D. C., p. 242.

4. Korth, M. W. et al., Effect of Hydrocarbon to Oxides of Nitrogen Ratios on Irradiated Auto Exhaust, Part I, JAPCA, 14:168-175, May 1964.

5. Hass, G. C., Application of Laboratory Data to Oxides of Nitrogen Standards, California Department of Public Health. (Presented at the Western Regional Meeting of the American Chemical Society, Los Angeles, California, November 19, 1965.)

6. Romanovsky, J. C., and Ingels, R. M., Effects of Changing Hydrocarbon and Nitric Oxide Levels on Eye Irritation, California Vehicle Pollution Laboratory, Los Angeles, California. (Presented at the Western Regional Meeting of the American Chemical Society, Los Angeles, California, November 19, 1965.)

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D. THE STATUS OF THE PROBLEM TODAY

I. Remaining unsolved problems. The previous discussion has attempted to summarize the various facets of the vehicle pollution problem from the standpoint of both effects on community atmospheres nationwide and the source of variables. In summary, the problems that remain today encompass a number of considerations, which may be enumerated as follows:

A. The importance of the diesel problem as it relates to smoke and odor control, the means for securing reduction of smoke and odors, and the development of test procedures for the setting of standards.

B. The importance of relative reactivity of the various organic species, particularly hydrocarbons, and the effects of reactivity on both standards and control methods.

C. The importance of various emission sources (exhaust, crankcase ventilation, fuel tank evaporation and carburetor evaporation losses) in relation to reactivity and need for control and the development of test procedures for these sources from all types of vehicles (passenger cars, trucks and buses).

D. The need for control of nitrogen oxides from vehicular sources, both gasoline engine and diesel engine power sources and concurrently for stationary sources.

E. The importance of instrumentation in measurement of pollution parameters for research, enforcement (certification) procedures, surveillance and inspection.

F. The problems of maintenance of devices on vehicles to insure their continued operation (surveillance and inspection), and/or the upgrading of such devices such that they will be essentially maintenance free.

G. The importance of in-traffic carbon monoxide levels, particularly their significance relative to driver fatigue.

II. The outlook in California. A study recently completed by the California State Department of Public Health depicts the typical story of how an increase in the pollution "base" negates cleanup efforts when measured against improvement in present levels. Fig. D-1 indicates the effect of various control programs on hydrocarbon emissions from motor vehicles in Los Angeles County, 1940-1980 (1). Note conditions under a) no control, b) the effect of crankcase controls starting with new cars for the 1961 model year, and applied to some pre 1961 model cars starting in 1964, c) the effect of exhaust controls starting with the 1966 model-year, d) the effect of stiffening of exhaust controls with the 1970 model-year, and e) additional effect of evaporation controls. Note that the goal is for reduction back to 1940 levels, and that this will only be met by application of controls over all vehicular emission sources.

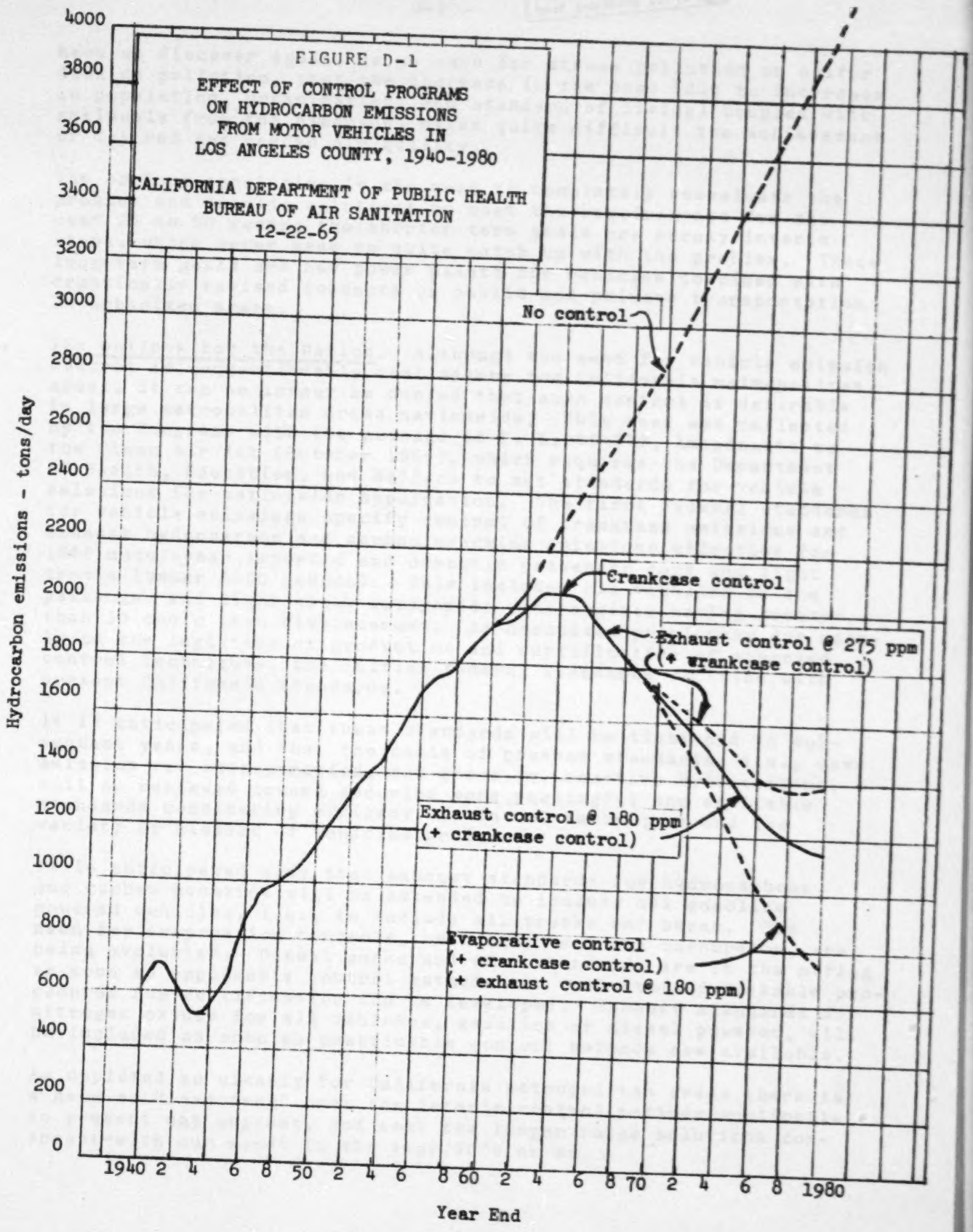
FIGURE D-1
EFFECT OF CONTROL PROGRAMS
ON HYDROCARBON EMISSIONS
FROM MOTOR VEHICLES IN
LOS ANGELES COUNTY, 1940-1980
CALIFORNIA DEPARTMENT OF PUBLIC HEALTH
BUREAU OF AIR SANITATION
12-22-65
No control
Crankcase control
Exhaust control @ 275 ppm
(+ crankcase control)
Exhaust control @ 180 ppm
(+ crankcase control)
Evaporative control
(+ crankcase control)
(+ exhaust control @ 180 ppm)
Hydrocarbon emissions - tons/day
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
1940 2 4 6 8 50 2 4 6 8 60 2 4 6 8 70 2 4 6 8 1980
Year End

FIGURE D-1

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Here we discover again, as we have for stream pollution or sulfur dioxide pollution, that the increase in the base (due to increases in population, urbanization, and standard of living) coupled with residuals from the clean-up, makes quite difficult the achievement of desired and needed air quality.

The obvious conclusion is the need to completely reevaluate the problem and provide solutions to meet the requirements for the next 25 to 50 years; the shorter term goals are merely interim steps, which never seem to quite catch up with the problem. These long-term goals are new power plants for vehicles combined with drastically revised concepts of public and private transportation in urbanized areas.

III. The outlook for the Nation. Although the need for vehicle emission control is unquestionably most severe for California metropolitan areas, it can no longer be denied that such control is desirable in large metropolitan areas nationwide. This need was reflected by the Congress with the passage of P. L. 89-272, Amendments to the Clean Air Act (October 1965), which requires the Department of Health, Education, and Welfare to set standards for vehicle emissions for nationwide application. The first Federal standards for vehicle emissions specify control of crankcase emissions and exhaust hydrocarbon and carbon monoxide emissions effective for 1968 model-year imported and domestic passenger cars and light trucks (under 6000 pounds). This includes all vehicles in the passenger and light truck categories with engines having greater than 50 cubic inch displacement. As discussed previously due mainly to the logistics of production and certification of approved control techniques, the initial federal standards coincide with present California standards.

It is anticipated that these standards will be tightened in subsequent years, and that the basis of present standards, i.e., mass emission vs. concentration, and gross vs. reactive hydrocarbons, will be reviewed toward securing more meaningful and equitable standards considering efficacy of control techniques and the variety of classes of vehicles produced.

It is anticipated also that exhaust standards for hydrocarbons and carbon monoxide will be extended to include all gasoline powered vehicles, i.e., to include all trucks and buses. The need for evaporation controls, both fuel tank and carburetor, are being evaluated. Diesel smoke and odor standards are in the offing as soon as applicable control methods are evaluated and workable procedures for certification can be developed. Exhaust standards for nitrogen oxides for all vehicles, gasoline or diesel powered, will be included as soon as practicable control methods are available.

As depicted so clearly for California metropolitan areas there is a need to "leap frog" over the interim control methods applicable to present day engines, and seek the longer range solutions consonant with our needs in the year 2000 or so.

References (Section D)

1. Effects of Control Programs on the Emissions of Hydrocarbon and Carbon Monoxide in Los Angeles County, California State Department of Public Health, Berkeley, California, January 1966.

ADDENDUM (1968)

to the

Seminar on Air Pollution by Motor Vehicles-1967

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2/10/68

Addendum (1968)

to the

Seminar on Air Pollution by Motor Vehicle - 1967

1. Proposed Federal Standards for 1970 Model Year Vehicle -- On January 4, 1968, the Secretary of HEW published in the Federal Register (Volume 33, No. 2, Part II) proposed 1970 standards for control of air pollution from new motor vehicles and new motor vehicle engines. Comments on these standards by interested persons, due originally 30 days after the original publication date, has been extended for an additional month's period.

2. Classes of Emissions Included in Proposed Standards -- The proposed 1970 model-year standards continue one standard effective for 1968 model-year vehicles tighten the standards on degree of control required on others and in addition, specify standards for classes of emissions or vehicles not included in the 1968 model-year standards. In summary the new standards are as follows:

   a. Crankcase Emissions from Automobiles and Light Trucks -- No change from 1968 standards 100% control is required for all gasoline-powered vehicles except motorcycles.

   b. Exhaust Emissions from Automobiles and Light Trucks -- The proposed 1970 standards are tighter than the 1968 standards. Standards are expressed in terms of mass emissions per mile and set uniformly for all car sizes at 2.2 grams of hydrocarbons per mile and 23 grams of carbon monoxide per mile. (Detailed discussion of this standard is included in Section 3 below.) The standard is not applicable to motorcycles or automobiles with an engine displacement of less than 50 cubic inches.

   c. Evaporation from Automobiles and Light Trucks -- The proposed standards for hydrocarbon emissions from gasoline tanks and carburetors for automobiles and light trucks has been set at "6 grams per test." The test procedure specified in the standards is intended to reproduce losses (fuel tank breathing losses and hot soak losses) during diurnal temperature fluctuations and driving practices comparable to those encountered during periods of the year when evaporation emissions are critical e.g., late summer and fall. The proposed standards would result in control of about 90% of the evaporation losses now discharged to the atmosphere.

   d. Exhaust Emissions from Gasoline-Powered Heavy Trucks and Buses -- The proposed standards would limit discharge of hydrocarbons to 275 ppm and carbon monoxide to 1.5% by volume similar to standards effective in California for 1969 model-year cars. The test cycle proposed is performed on an engine or chassis dynamometer. The

standard would require about 35% control of hydrocarbons and 37% control of carbon monoxide. As is obvious from reductions required for trucks and buses in comparison to automobiles, heavy truck and bus standards in all likelihood will be tightened markedly in future years.

e. Smoke from Diesel-Powered Vehicles -- The proposed standards specify that light transmission shall not be reduced by more than 20% except that reductions of not more than 40% for a total of not more than 5 seconds shall be permitted during the running of the two dynamometer test cycles.

3. Proposed Revised Standards for Exhaust Emissions from Automobiles and Light Trucks

a. In general the proposed standards (2.2 grams of hydrocarbon and 23 grams of carbon monoxide per vehicle mile), which would replace standards effective with the 1968 model year, would lower by about one-third the 1968 level of allowable automobile exhaust pollutants by requiring 77% control of hydrocarbons and 68% control of carbon monoxide. In general, a typical uncontrolled vehicle, prior to the 1968 standards, emitted 9.7 grams of hydrocarbons and 71 grams of carbon monoxide per vehicle mile. It should be recognized that these figures are based on a very nebulous definition of a "typical uncontrolled vehicle," which is as difficult to define as a typical human being or any other member of a diverse population.

b. Equity of Mass Emission Standards -- The proposed standards, based on single mass emission per mile values for hydrocarbons and carbon monoxide for all weights of vehicles, recognize the equity of allowing all vehicle owners to pollute the air an equal amount for their personal transportation needs. The 1968 standards recognized this equity in part by setting standards in terms of 3 engine displacement categories (hydrocarbons 410, 350 and 275 ppm and carbon monoxide 2.3, 2.0 and 1.5% for the engine displacement classes 50-100, 100-140 and greater than 140 cubic inches respectively). The 1970 standards, in recognition of this principle across-the-board, will require greater improvements over 1968 standards for heavier vehicles than it does for lighter vehicles.

c. Inertial Wheel Weight -- The certification tests in the proposed new standards provide for computation of mass emissions based on the inertial wheel weight used in testing the car which inertial wheel weight is selected in accordance with the "loaded vehicle weight" (specified as the published shipping weight plus 400 pounds). This procedure recognizes that emissions are related to loading, and that the loading during certification tests is provided solely by the inertial wheel weight.

d. Exhaust Volume -- The proposed standards provide for the measurement of average concentration of emission over the specified test cycle consisting of various modes of driving. Inherent in these

modes are speeds and times resulting in a total equivalent distance traveled over the complete cycle. To convert from concentration to mass emission, it is necessary to know the exhaust volume. This is provided for in the standards by a computational procedure based on the dynamometer inertial wheel weight. The logic of this procedure stems from the fact that exhaust volume is primarily a function of the work done by the engine which for certification test, is work done driving the car on the dynamometer loaded with the inertial wheel. The conversion formula is as follows: Exhaust Volume (cu.ft./mile) = $-11.54+0.0281W-0.00000193W^2$ where W is the inertial wheel weight in pounds. In the computation of mass emissions for hydrocarbons, factors are also required to convert hydrocarbon concentrations on a molar basis as hexane, as measured by the non-dispersive infrared analyzer, to a carbon number basis, and to convert the hydrocarbon detected by the infrared analyzer to total hydrocarbons in the exhaust gas.

e. Comparison of 1968 and 1970 Standards -- Although a specific comparison of the 1968 and 1970 standards is not possible across-the-board as there is no consistent relation between engine displacement and loaded vehicle weight (this varies for each car), Figures S-1 and S-2 do give a general comparison that is valid except for some cars falling close to class cut-off points specified in either of the two standards. Note in general reduction below 1968 standards required by the 1970 standards for the heavier cars in comparison to light cars. As additional point not noted on these curves is that manufacturers are permitted to average all cars which they produce that fall into a given inertial weight class. Figure S-3 shows a comparison of 1968 and 1970 emission standards for specific vehicles. Note that a Lincoln weighing 5654 pounds will have to meet equivalent concentration standards of 150 ppm hydrocarbon and 0.85% carbon monoxide compared to 340 ppm and 2.3% for a Renault weighing 2030 pounds.

f. Involvement of Test Procedures in 1970 Standards -- As has been indicated above, the 1970 mass emission standards, although reflecting the mass emission concept, do not in fact incorporate this principle in its entirety. The 1970 standards are a compromise based on the exigence of retaining the instruments and procedures for certification contained in the 1968 standards. Future standards will incorporate measurement of exhaust volume that will then allow the full implementation of this concept.

4. State of California Activities -- The State of California Board of Health initiated its program of adopting standards for motor vehicle emissions in 1959. In 1961 the State of California Motor Vehicle Pollution Control Board began its program for certifying emission controls to meet the standards set by the Board of Health. As a result of these activities, installation of devices to control crankcase ventilation began in California late in 1960 (1961

model-year cars) and devices for control of hydrocarbons and carbon monoxide in exhaust began in late 1965 (1966 model-year cars). During the past year under new legislation passed by the Assembly, all air pollution control activities in the State of California, including motor vehicles have been placed under the direction of a newly created California Air Resources Board. The Board, comprised of 14 members appointed by the Governor, held its first meeting on February 8, 1968.

The Air Quality Act of 1967 preempts States from enacting regulations to control emissions from motor vehicles except for those States (California is the only one) that had adopted regulations prior to March 30, 1966. In accordance with this provision in the Air Quality Act of 1967, the Department of Health, Education and Welfare held hearings in California starting on January 15, 1968, to ascertain whether more stringent regulations in California are required. As of this date (February 18, 1968) the hearings have not as yet been closed and hence rulings on the hearings have not been made.

GENERAL COMPARISON ON A CONCENTRATION BASIS OF 1968 STANDARDS AND PROPOSED 1970 STANDARDS (1/4/68) - CARBON MONOXIDE

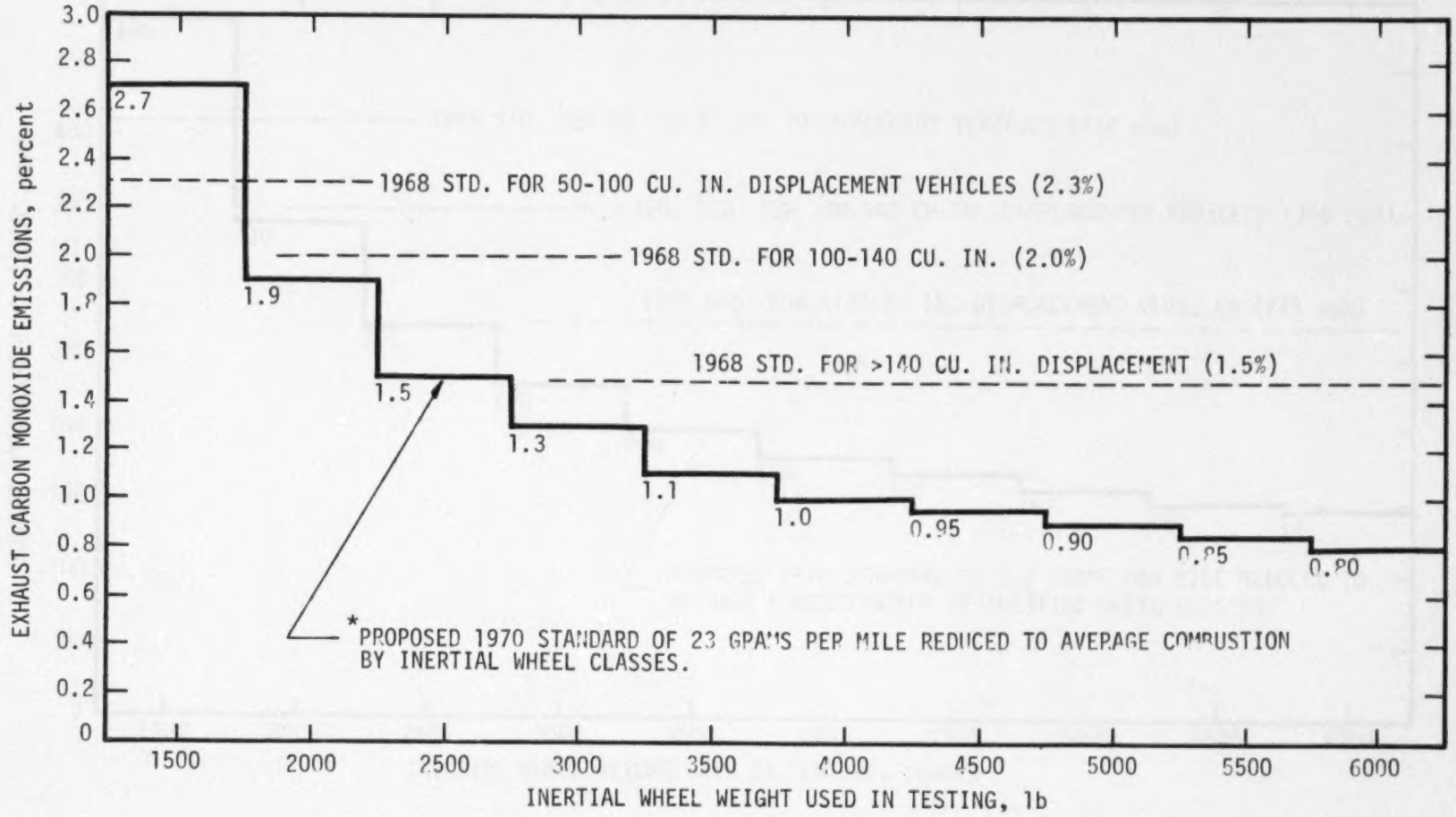

FIGURE S-1

GENERAL COMPARISON ON A CONCENTRATION BASIS OF 1968 STANDARDS AND PROPOSED 1970 STANDARDS (1/4/68) - HYDROCARBONS

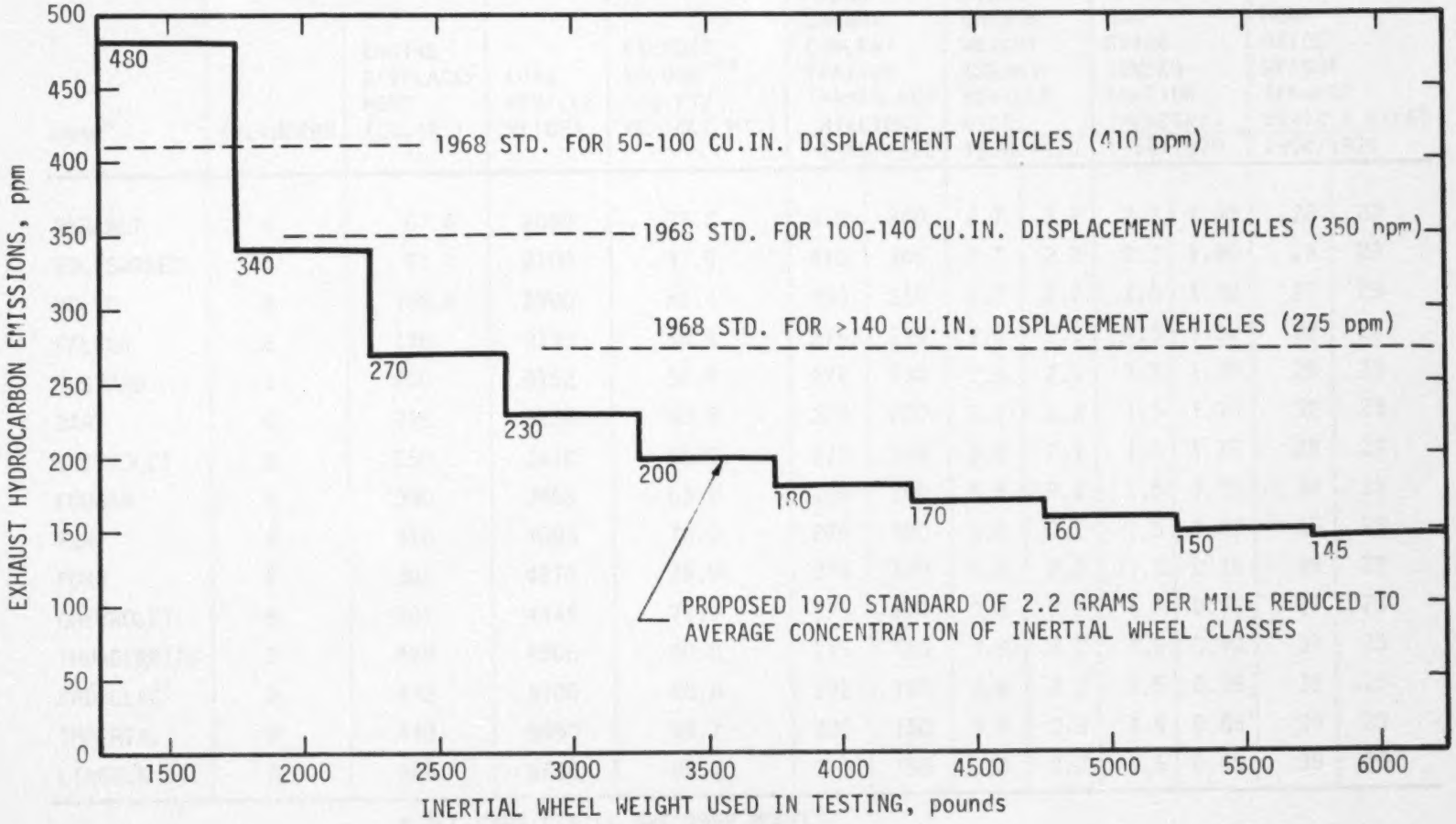

FIGURE S-2

FEDERAL EXHAUST EMISSION STANDARDS PROPOSED FOR 1970 CARS AS COMPARED TO STANDARDS IN EFFECT FOR 1968 AND 1969 CARS

NAME*	CYLINDERS	ENGINE DISPLACEMENT (CU.IN.)	LOAD VEHICLE WEIGHT	EXHAUST VOLUME ** (CU.FT/ VEHICLE MI.)	HYDROCARBON CONCENTRATION (PARTS PER MILLION)		HYDROCARBON WEIGHT (GRAMS/ VEHICLE MILE)		CARBON MONOXIDE CONCENTRATION (PERCENT)		CARBON MONOXIDE WEIGHT (GRAMS/ VEHICLE MILE)	
					1968/1970		1968/1970		1968/1970		1968/1970	
RENAULT	4	67.6	2030	37.0	410	340	2.7	2.2	2.3	1.90	28	23
VOLKSWAGEN	4	91.1	2100	37.0	410	340	2.7	2.2	2.3	1.90	28	23
VOLVO	4	108.6	2900	55.4	350	230	2.7	2.2	2.0	1.30	29	23
FALCON	6	170	3130	55.4	275	230	2.5	2.2	1.5	1.30	26	23
MUSTANG	6	200	3152	55.4	275	230	2.5	2.2	1.5	1.30	26	23
DART	6	275	3258	63.2	275	200	3.1	2.2	1.5	1.10	32	23
CHEVROLET	6	250	3450	63.2	275	200	2.8	2.2	1.5	1.10	29	23
COUGAR	8	390	3463	63.2	275	200	3.6	2.2	1.5	1.10	37	23
FURY	8	318	4093	70.0	275	180	3.3	2.2	1.5	1.00	35	23
FORD	8	302	4270	75.9	275	170	3.3	2.2	1.5	0.95	35	23
CHEVROLET	8	307	4448	75.9	275	170	3.3	2.2	1.5	0.95	35	23
THUNDERBIRD	8	429	4806	80.8	275	160	3.8	2.2	1.5	0.90	39	23
CADILLAC	8	472	5100	80.8	275	160	3.8	2.2	1.5	0.95	39	23
IMPERIAL	8	440	5450	84.7	275	150	3.8	2.2	1.5	0.85	39	23
LINCOLN	8	460	5654	84.7	275	150	3.8	2.2	1.5	0.85	39	23

* ALL CARS LISTED ARE 1968 MODELS

** CALCULATED FROM VEHICLE WEIGHT

FIGURE S-3